高性能MgB2超伝導線材に関する研究

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Development of high performance MgB₂ superconducting wires
(高性能MgB₂超伝導線材に関する研究)

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Abstract

MgB$_2$ is expected to be used in no-helium conditions to replace metallic superconductors that are operating in a liquid helium environment. Low cost is the most important advantage of MgB$_2$ to be used as a practical superconducting wire. Currently, there have already been products using MgB$_2$ superconductor, but the cost per unit length and unit superconducting current density of these products are not so low because the critical current properties of these MgB$_2$ wires are not high enough to operate in the expected condition. The expected condition for MgB$_2$ wire operation is at ~20 K using a cryocooler or liquid hydrogen. The main work of this thesis is to enhance the critical current properties for MgB$_2$ wires at 20 K and 5 T.

Internal-Mg-diffusion (IMD) process produces higher density MgB$_2$ layer than that of Powder-in-tube (PIT) process, thus IMD MgB$_2$ wires have higher critical current properties. However, un-reacted B particles were observed in the MgB$_2$ layer of IMD-processed wires fabricated with low quality B powder (325-mesh, 99%). In chapter 2, I found that some Mg powder addition is effective to decrease the un-reacted B particles and enhance the critical current density ($J_c$) values. On the other hand, Mg powder addition also formed voids in MgB$_2$ layer and these voids decreased the $J_c$ values. If the amount of Mg powder in the B layer is increased, the Mg rod diameter should be decreased simultaneously in order to maintain a Mg:B ratio of 1:2, corresponding to stoichiometric MgB$_2$. Consequently I developed a new hybrid method for fabricating MgB$_2$ wires by a combination of IMD and PIT processes. The MgB$_2$ layer thickness is larger and the diameter of the central hole is smaller than those of a conventional IMD processed wire, thus MgB$_2$ area fraction is higher. The proposed method also achieves a much higher MgB$_2$ layer density, and thus a much higher $J_c$, than those obtained by the PIT method. The combination of these factors leads to the enhanced engineering critical current density ($J_{c_{\text{e}}}$) value. The new method introduced in chapter 2 is developed for the low quality B powder, but it is also effective for nano-sized B high quality powders used in chapter 5 and in chapter 6 because it could be effectively used to decrease the B-rich region caused by these nano-sized powders.

The multi-filamentary superconducting wires are important for practical applications. In chapter 3, we succeeded in fabricating IMD-processed 37-filamentary MgB$_2$ wires. SiC-added 37-filamentary MgB$_2$ wires show the highest $J_{c_{\text{e}}}$ value (7.6 x 10$^4$ A/cm$^2$ at 4.2 K and 10 T) among all of the IMD-processed MgB$_2$ wires fabricated under the same conditions (mono-filamentary and 7-filamentary). The short Mg diffusion distance of 37-filamentary IMD-processed MgB$_2$ wires decreases un-reacted B particles. This is the main factor to raise the $J_c$ values. The successful fabrication of 37-filamentary wires indicates that the IMD process can be used to fabricate MgB$_2$ wires for large-scale applications.

It was reported that the co-addition of SiC and ethyltoluene is effective in the PIT-processed MgB$_2$ wires. Accordingly, it may be also effective in the IMD-processed MgB$_2$ wires. In chapter 4, I...
have carried out the SiC and ethyltoluene, toluene, or dimethylbenzene co-addition to IMD-processed MgB₂ wires. The \( J_c \) properties are enhanced by the toluene and dimethylbenzene, but not so good for ethyltoluene.

The researchers in Ohio State University and Hyper Tech Company used a special plasma-synthesized 2% carbon-coated B powder (Special Materials Inc., SMI powder) to fabricate thin IMD-processed MgB₂ wires (diameter: 0.55 mm). They obtained high \( J_c \) and \( J_e \) for different samples. The small diameter of the wire is considered to decrease the Mg diffusion distance, which leads to an improved reaction between Mg and B, thus a high \( J_c \) is obtained. I also tried this B powder, however, I could not obtain good results as theirs. After investigating the B powder, I found that many BCl₃ (source material for this B powder) exists in the B powder. Since dimethylbenzene dissolve BCl₃, and our experiments in chapter 2 also showed dimethylbenzene enhanced the \( J_c \) of IMD-processed MgB₂ wires, I used the dimethylbenzene to remove BCl₃ from the B powder. The dimethylbenzene decreased the BCl₃ in B powder and then I obtained \( J_c \) values higher than Ohio state university in chapter 5. For both Ta- and Fe-sheathed wires, the highest \( J_c \) value was about \( 1.2 \times 10^5 \text{ A/cm}^2 \) at 4.2 K and 10 T, and the \( J_e \) value was about \( 1 \times 10^4 \text{ A/cm}^2 \). Furthermore, the Fe-sheathed wire exhibited a \( J_c \) of \( 7.6 \times 10^4 \text{ A/cm}^2 \) and a \( J_e \) of \( 5.3 \times 10^3 \text{ A/cm}^2 \) at 20 K and 5 T, which are the highest values reported for MgB₂ wires to date.

The carbon-coated nano-sized B powder is responsible to obtain the high \( J_c \) and \( J_e \) for IMD-processed MgB₂ wires. However, the C-coating process using plasma method is not easy, thus it is expensive. Furthermore, this B powder is unstable because BCl₃ exists. Therefore, I tried a new B powder added with an aromatic hydrocarbon (coronene, \( C_{24}H_{12} \)) as a carbon source, which is described in chapter 6. The similar level of high \( J_c \) and \( J_e \) values to the carbon-coated B powders in chapter 5 were obtained. The \( J_c \) properties are expected to be further enhanced by optimizing the coronene-coating and heat treatment conditions. It is easy to obtain this coronene-coated B powder and the powder is stable. And the amount of carbon addition is also easily controlled. Using the new B powder with \( C_{24}H_{12} \) coating we can expect to fabricate high performance MgB₂ wires for large-scale practical applications with low cost.
Figure captions

Chapter 1

Fig. 1-1 Brief history of discovery of superconductors .............................................................. 3

Fig. 1-2 The properties of a superconducting material ............................................................. 4

Fig. 1-3 Crystal structure of MgB₂ .............................................................................................. 7

Fig. 1-4 Fabrication of MgB₂ wires with PIT process .............................................................. 8

Fig. 1-5 Fabrication of MgB₂ wires by IMD process ............................................................... 9

Fig. 1-6 Typical optical microscopy of cross sectional images of IMD-processed MgB₂ wire with diameter of 1.2 mm by optical microscopy, (a) transverse and (b) longitudinal cross section before heat treatment, (c) transverse and (d) longitudinal cross section after heat treatment .............. 10

Fig. 1-7 The uniformity in longitudinal direction of the several IMD-processed MgB₂ wires ....... 11

Fig. 1-8 Typical SEM image of MgB₂ wires (a) IMD processed MgB₂ wires, (b) PIT processed MgB₂ wires ........................................................................................................................................ 11

Chapter 2

Fig. 2-1 Schematic maps of the transverse cross sections for MgB₂ wires fabricated with (a) IMD, (b) PIT, and (c) a new method combining IMD and PIT .................................................................................. 20

Fig. 2-2 (a) \( J_c \)-B curves and (b) \( J_e \)-B curves of IMD undoped and Mg-added MgB₂ wires .............. 23

Fig. 2-3 Magnified optical microscope images of transverse cross-section of IMD-processed (a) undoped and (b) 6 mol% Mg-added MgB₂ wires .................................................................................. 24

Fig. 2-4 SEM images of longitudinal cross-section of IMD-processed (a) undoped and (b) 6 mol% Mg-added MgB₂ wires ......................................................................................................... 25

Fig. 2-5 (a) STEM dark field (DF) image of the reacted layer in undoped MgB₂ wire. (b) Magnified STEM-DF image of the red frame in Fig 4(a). (c) High resolution image of region (A) in Fig 4(b). (d) High resolution image of region (B) in Fig 4(b) .................................................................................. 26

Fig. 2-6 STEM-DF image of 6 mol% Mg-added IMD-processed MgB₂ wires ............................ 27

Fig. 2-7 \( J_c \) value at 4.2 K and 10 T as a function of Mg concentration of IMD MgB₂ wires ......... 27
Chapter 3

Fig. 3-1 Fabrication process of 37-filamentary IMD-processed MgB₂ wires .................................. 39

Fig. 3-2 Heat treatment processes for IMD-processed 37-filament MgB₂ wires ....................... 39

Fig. 3-3 (a) SEM images of IMD-processed 37-filament MgB₂ wires and its filaments, and (b) the elements mapping for one filament of (a) ................................................................. 41

Fig. 3-4 (a) Jₑ values at 4.2 K and 10 T, and (b) Jₑ-B curves at 4.2 K for several heat treatment conditions of the IMD-processed 37-filament MgB₂ wires ......................................................... 42

Fig. 3-5 Jₑ-B curves of the IMD-processed MgB₂ wires with different filaments at 4.2 K ............ 44

Fig. 3-6 SEM images in transverse cross-section of Ta-mono (a) near Ta sheath and (b) near hole (spectrum are observed for spots 1, 2 and 3), (c) Ta-37 filament 1, and (d) Ta-37 filament 2 ...... 45

Fig. 3-7 Temperature dependence of the Jₑ-B curve for (a) SiC-added, (b) both undoped and SiC-added IMD-processed 37-filament MgB₂ wires, and (c) temperature dependence of Jₑ on the
temperature (higher than 30 K) at the self-field for both undoped and SiC-added IMD-processed 37-filament MgB$_2$ wires .......................................................................................................................................................... 48

Chapter 4

Fig. 4-1 $J_c$–B curves (at 4.2 K) of various IMD-processed MgB$_2$ wires heat treated at (a) 640°C, (b) 670°C and (c) 700°C for 3 hours, and (d) $J_c$–B curves (at 4.2 K) of various IMD processed MgB$_2$ wires: optimized heat treatment temperature was chosen for each wire ................................................................................................. 54

Fig. 4-2 (a) the $J_c$–B curves and (b) the $J_c$–B curves of SiC+dimethylbenzene co-added IMD-processed MgB$_2$ wires, respectively. (c) the $J_c$–B curves of pure IMD-processed MgB$_2$ wires ........... 56

Fig. 4-3 $J_c$–B curves of IMD-processed MgB$_2$ wires with different additives ................................................. 57

Fig. 4-4 XRD patterns of IMD-processed MgB$_2$ wires with different additives .......................... 58

Fig. 4-5 SEM images of IMD-processed MgB$_2$ wires (a) with no addition, (b) with toluene-addition, (c) with SiC-addition, (d) with both SiC and toluene co-addition ................................................................. 59

Fig. 4-6 Representative SEM image(a), EDX element mapping images of B, O, Mg, Si and C elements (b - f), on the longitudinal cross sections of SiC-added IMD-processed MgB$_2$ wires ...... 60

Fig. 4-7 (a) TEM image of IMD-processed mono-core MgB$_2$ wires with SiC addition, (b) high resolution image of region B in (a), (c) diffraction pattern of (b), (d) high resolution image of region C in (a), (e) diffraction pattern of (d) .......................................................................................................................... 61

Fig. 4-8 Elemental maps by EDS and EFI of (a) pure wires and (b) SiC-added wires; the schematic illustrations of the elemental distributions of (c) pure wires and (d) SiC-added wires .......... 63

Chapter 5

Fig. 5-1 The pretreating process for SMI B powder by dimethylbenzene ................................................. 67

Fig. 5-2 XRD pattern of IMD-processed MgB$_2$ wires (before heat treatment) fabricated with SMI powder (left), and the images of IMD-processed MgB$_2$ wires fabricated with SMI and SMI+D powders (right) .................................................................................................................................................. 68

Fig. 5-3 EDX spectra of (a) SMI powder, and (b) SMI+D powder .............................................................. 69

Fig. 5-4 SEM images of (a) SMI powder, and (b) SMI+D powder .................................................................... 70
Fig. 5-5 Cross-sectional SEM images of (a), (b) Ta-SMI+D wire, and (c), (d) Fe-SMI+D-1wire, (e-f) optical microscope images of (c-d) ........................................................................................................ 71

Fig. 5-6 X-ray diffraction (XRD) patterns for the Fe-SMI and Fe-SMI+D-1 wires ...................... 72

Fig. 5-7 Comparison of (a) Jc-B, and (b) Jc-B curves for IMD-processed MgB2 wires at 4.2 K ........ 74

Fig. 5-8 (a) Jc-B curves and (b) Je-B curves for IMD-processed MgB2 wire (Fe-SMI+D-1) at different temperatures. Previously reported data for Ta-sheathed wire fabricated using SiC addition [7, 8], and Jc data for Nb-Ti wires [12] are shown using dotted lines ................................................................. 76

Fig. 5-9 SEM images of Fe-SMI wire at magnification of (a) 30k, and (b) 80k times, and (c) EDX maps corresponding to the area shown in (a). SEM images of Fe-SMI+D-1 wire at magnification of (d) 30k and (e) 80k times. SEM images of Ta-SMI+D wire at magnification of (f) 30k and (g) 50k times ... 78

Fig. 5-10 (a) STEM dark-field image of Ta-SMI+D wire at 25k times magnification and camera length of 20 cm, (b) STEM dark-field image of region R1 in (a) at 250k times magnification and camera length of 20 cm, (c) STEM bright-field image of region R2 in (a) at 300k times magnification and camera length of 80 cm, (d) STEM dark-field image of region R2 in (a) at 300k times magnification and camera length of 80 cm, (e) high resolution images (800k) and corresponding fast Fourier transforms (FFT) of regions A to E in (c) and (d), and (f) electron energy loss spectroscopy (EELS) images of region R3 in (a) ........................................................................................................ 81

Chapter 6

Fig. 6-1 Molecule structure of coronene (C24H12) .................................................................................. 85

Fig. 6-2 Transverse cross sectional image observed by optical microscope (a), and longitudinal cross sectional image observed by SEM (b) of PIT-processed MgB2 wires (diameter: 1.0 mm) ... 86

Fig. 6-3 (a) Jc-B curves, and (b) Jc-B curves of PIT-processed MgB2 wires at 4.2 K ....................... 87

Fig. 6-4 X-ray diffraction patterns of PIT-processed MgB2 wires ...................................................... 88

Fig. 6-5 SEM images of (a) undoped, (b) 2%, (c) 5%, and (d) 10% coronene-added PIT-processed MgB2 wires ........................................................................................................................................ 89

Fig. 6-6 Optical microscope image on the transverse cross section of the IMD-processed MgB2 wires (diameter: 0.6 mm) ........................................................................................................ 90

Fig. 6-7 (a) Jc-B curves, and (b) Jc-B curves of IMD-processed MgB2 wires ................................... 91
Fig. 6-8 The $J_c$ values at high magnetic fields of undoped and coronene-added MgB$_2$ wires fabricated with both IMD and PIT processes ........................................................................................................ 92

Chapter 7

Fig. 7-1 Photograph (left) and schematic illustration (right) of apparatus to measure $I_c$ versus uniaxial tension........................................................................................................................................... 98

Fig. 7-2 $I_c$ as a function of uniaxial strain, inset shows $I_c/I_{c0}$ as a function of uniaxial strain (both IMD and PIT are fabricated with 325-mesh B with 10 mol% SiC addition as the method introduced in chapter 4) ........................................................................................................................................... 99

Fig. 7-3 schematic illustration (left) and photo (right) of apparatus to measure $I_c$ versus transverse compression ........................................................................................................................................... 100

Fig. 7-4 Normalized $I_c$ as a function of transverse compressive stress ................................................. 100

Fig. 7-5 (a) The diffractometer and (b) experiment layout ............................................................................. 101

Fig. 7-6 The relations of a load strain and the lattice strain ........................................................................ 101

Fig. 7-7 (a) Experimental equipment, (b) magnified image, and (c) wire furnace ................................. 102

Fig. 7-8 (a) 2-D data of XRD diffraction, and (b) 1-D data of XRD calculated from (a) ..................... 103
Table captions

Chapter 1
Table 1-1 Important superconducting materials for the development of superconducting wires....6

Chapter 2
Table 2-1. The specifications of all MgB₂ wires .................................................................................. 21
Table 2-2. Details of the fabricated wires .......................................................................................... 30

Chapter 3
Table 3-1. The details of compared wires in Fig. 4 ........................................................................... 44
Table 3-2. The characteristic element spectrum details of B (B k), C (C k), Mg (Mg k) and Si (Si k) for Fig. 5(b) ........................................................................................................................................ 46

Chapter 4
Table 4-1. The a-axis, c axis, and amount of carbon substitution for boron of IMD-processed mono-core MgB₂ wires with different additives ............................................................................. 58

Chapter 5
Table 5-1. Compositions of SMI and SMI+D powders obtained from EDX analysis ....................... 69
Table 5-2. MgB₂ area fraction and sheath area fraction for high-performance MgB₂ wires ........... 71
Table 5-3. Lattice parameters, amount of carbon substitution for boron, and calculated and measured $T_{ic}$ for Fe-sheathed wires fabricated using SMI and SMI+D powders ............................ 72

Chapter 6
Table 6-1 The properties of PIT-processed MgB₂ wires in this experiment ................................. 88
Contents

Chapter 1 Introduction........................................................................................................................ 1
  1.1 Superconductivity........................................................................................................................ 1
    1.1.1 History ................................................................................................................................ 1
    1.1.2 Superconducting properties and applications ................................................................. 4
    1.1.3 Superconducting materials ............................................................................................... 5
  1.2 MgB₂ ......................................................................................................................................... 7
    1.2.1 Characteristics of MgB₂ superconductor ......................................................................... 7
    1.2.2 MgB₂ superconducting wires ......................................................................................... 8
    1.2.3 Internal Mg diffusion process ....................................................................................... 9
  1.3 Thesis content ............................................................................................................................ 12
    1.3.1 Research purpose, theory, and research methods .......................................................... 12
    1.3.2 The characterization methods ....................................................................................... 14
    1.3.3 The research experience and thesis structure ................................................................ 15
Chapter 2 Development of a new method combining IMD and PIT processes for MgB₂ wires .... 20
  2.1 Introduction............................................................................................................................. 20
  2.2 Enhancement of critical current properties of IMD-processed MgB₂ wires by Mg addition .. 21
    2.2.1 Experimental details ...................................................................................................... 21
    2.2.2 Results and discussion ................................................................................................. 22
  2.3 Fabrication of MgB₂ wires with a new method combining IMD and PIT processes .......... 30
    2.3.1 Experimental details ...................................................................................................... 30
    2.3.2 Results and discussion ................................................................................................. 31
  2.4 Conclusions............................................................................................................................. 36
Chapter 3 Fabrication of 37-filamentary IMD-processed MgB₂ wires ........................................ 38
  3.1 Introduction............................................................................................................................. 38
  3.2 Experimental details ............................................................................................................... 38
  3.3 Results and discussion .......................................................................................................... 40
  3.4 Conclusions............................................................................................................................. 48
Chapter 4 Enhancement of critical current properties of IMD-processed MgB₂ wires by SiC and liquid aromatic hydrocarbon co-addition ................................................................. 50
  4.1 Introduction ........................................................................................................... 50
  4.2 Experimental details ............................................................................................. 50
  4.3 Results and discussion ......................................................................................... 51
    4.3.1 Enhancement of Jₙ and Jₜ for MgB₂ wires by SiC and liquid aromatic hydrocarbon co-addition ........................................................................................................ 51
    4.3.2 Study on the mechanism of the Jₙ enhancement of MgB₂ wires by SiC and toluene co-addition ........................................................................................................ 57
    4.3.3 The microstructure analysis and a proposal of new mechanism of enhanced Jₙ of MgB₂ wire by SiC addition .................................................................................. 60
  4.4 Conclusions ............................................................................................................ 64
Chapter 5 Enhancement of Jₙ properties of MgB₂ wires by pretreating carbon-coated nano-sized B powder with Dimethylbenzene ........................................................................ 66
  5.1 Introduction ............................................................................................................ 66
  5.2 Experimental details ............................................................................................. 66
  5.3 Results and Discussion ......................................................................................... 68
    5.3.1 Starting B powder ............................................................................................ 68
    5.3.2 Fabrication of wires ......................................................................................... 70
    5.3.3 Critical current properties ................................................................................ 73
    5.3.4 Scanning electron microscopy analysis ........................................................... 77
    5.3.5 Transmission electron microscopy analysis ..................................................... 79
  5.4 Conclusions ............................................................................................................ 82
Chapter 6 Enhancement of critical current properties of MgB₂ wires by aromatic hydrocarbon (C₂₄H₁₂) addition .................................................................................. 84
  6.1 Introduction ............................................................................................................ 84
  6.2 Experimental details ............................................................................................. 85
  6.3 Results and discussion ......................................................................................... 86
  6.4 Conclusions ............................................................................................................ 92
Chapter 7 Summary and prospects ............................................................................. 94
  7.1 Summary ............................................................................................................... 94
7.2 Some ongoing topics ........................................................................................................... 98
  7.2.1 The comparison of mechanical properties for IMD- and PIT-processed MgB₂ wires ...... 98
  7.2.2 Strain measurement of IMD-processed MgB₂ wires by synchrotron radiation at SPring-8 ........................................................................................................................................ 101
  7.2.3 Reaction observation of IMD-processed MgB₂ wires during the heat treatment by XRD in Spring-8 .................................................................................................................. 102
  7.3 Prospects ............................................................................................................................. 104
Publications ....................................................................................................................................... 107
Chapter 1 Introduction

1.1 Superconductivity

1.1.1 History

Superconductivity is a phenomenon of exactly zero electrical resistance and expulsion of magnetic fields occurring in certain materials when cooled below a characteristic critical temperature. In 1911, Heike Kamerlingh Onnes and his colleagues found that the resistivity of solid mercury abruptly disappeared at the temperature of 4.2 K [1]. He termed this phenomenon as "superconductivity".

In 1933 [2], the German physicists Walther Meissner and Robert Ochsenfeld discovered a phenomenon that superconductors expel applied magnetic fields by measuring the magnetic field distribution outside superconducting tin and lead samples. The samples were cooled in an applied magnetic field below their superconducting transition temperature. Below the transition temperature the samples cancelled nearly all interior magnetic fields. This phenomenon has come to be known as the Meissner effect. Heinz London and Fritz London showed that the Meissner effect was a consequence of the minimization of the electromagnetic free energy carried by superconducting current in 1935 [3]. So they proposed two equations that govern the microscopic electric and magnetic fields and termed as London equations. Brian Pippard introduced the notion of coherence length in superconductors in his proposal for the non-local generalisation of the Londons' equation concerning electrodynamics in superfluids and superconductors [4]. The non-local kernel proposed by Pippard can be deduced within the framework of the first microscopic theory-BCS theory of superconductivity. BCS theory was proposed by John Bardeen, Leon Neil Cooper, and John Robert Schrieffer in 1957 [5]. It is wonderfully summarized as [6]: an electron moving through a conductor will attract nearby positive charges in the lattice. This deformation of the lattice causes another electron (with opposite spin) to move into the region of higher positive charge density. The two electrons then become correlated (occupying states with equal and opposite momentum and spin) to form Cooper pairs. Because there are a lot of Cooper pairs in superconductor, these pairs overlap very strongly and form a highly collective condensate. In this "condensed" state, the breaking of one pair will change the energy of not only just a single electron or a single pair, but the entire condensate. Thus, the energy required to break any single pair is related to the energy required to break all of the pairs. Because the pairing increases this energy barrier, kicks from oscillating atoms in the conductor (which are small at sufficiently low temperatures) are not enough to affect the condensate as a whole, or any individual "member
pair” within the condensate. Thus the electrons stay paired together and resist all kicks, and the electron flow as a whole (the current through the superconductor) will not experience resistance.

Before the BCS theory, some other important theories of superconductivity were also devised. Maxwell and Reynolds et al. [7] found that the critical temperature of a superconductor depends on the isotopic mass of the constituent element in 1950. This important discovery pointed to the electron-phonon interaction as the microscopic mechanism responsible for superconductivity.

Also in 1950, Landau and Ginzburg [8] devised the Ginzburg-Landau theory, which combined Landau's theory of second-order phase transitions with a Schrödinger-like wave equation, had great success in explaining the macroscopic properties of superconductors. In particular, Abrikosov [9] predicted from Ginzburg-Landau theory that there are two categories of superconductors, which are now referred to as Type I and type-II superconductors. Ginzburg–Landau theory defines two parameters, the superconducting coherence length and the London magnetic field penetration depth to discuss the two types of superconductors. In a type-II superconductor, the coherence length is smaller than the penetration depth. This leads to the negative free energy of the interface between superconducting and normal phases. While for the type-I superconductor, the free energy is positive. These caused that the superconductivity of type-I superconductors are abruptly destroyed via a first order phase transition when the strength of the applied field rises above a critical value $H_c$. However, type-II superconductors have two critical magnetic fields. The first, lower critical field $(H_{c1})$ is the field at which magnetic flux vortices start to penetrate the material but the material remains superconducting outside of these microscopic vortices. When the vortex density becomes too large, the entire material becomes non-superconducting; this corresponds to an upper critical field $(H_{c2})$ [10, 11, 12]. Type-I superconductor is normally exhibited by pure metals, such as Hg, Sn and so on. Type-II superconductors are usually made of metal alloys or complex oxide ceramics. The applications of superconductor are usually related to magnetic fields, so only type-II superconductors are used for practical applications due to their high $H_{c2}$.

The type-II superconductors allow magnetic flux to enter in quantized packets surrounded by a superconducting current vortex. These sites of penetration are known as flux lines. The number of flux lines per unit area is proportional to the magnetic field with a constant of proportionality equal to the magnetic flux quantum. At low temperatures the flux lines are pinned in place and cannot move. These flux pinning prevent flux creep, which can create a pseudo-resistance and depress both critical current density and critical field [11, 12]. The flux pinning is a very important phenomenon for practical applications of type-II superconductors. At high temperatures depinning of flux lines “flux creep” occurs due to the thermal activation.

In 1962, the British physicist Brian David Josephson [13] found a macroscopic quantum phenomenon in superconductors, which is termed as Josephson effect. The Josephson effect is the
phenomenon of supercurrent—i.e. a current that flows indefinitely long without any voltage applied—across a device known as a Josephson junction (JJ), which consists of two superconductors coupled by a weak link (a thin insulating barrier, or a short section of non-superconducting metal). The Josephson effect has wide usages such as superconducting quantum interference devices (SQUID), single-electron transistor, and superconducting quantum computing.

During the development of the theory of superconductivity, discovery of new superconductors are also developed. Fig. 1-1 shows the brief history of discovery of superconductors. The superconducting transition temperature ($T_c$) is increasing by year. Three stages can be observed from the Fig. 1-1. First stage is before 1980s, the discovery is focus on pure metal and Nb-based compounds. Second stage is 1980-2000, the discovery of cuprates with high $T_c$ is a milestone for science. In 1986, Bednorz and Müller [14] discovered superconductivity in a lanthanum-based cuprate perovskite material, which had a transition temperature of 35 K (Nobel Prize in Physics, 1987). Soon after that, the YBCO [15] and Bi-based [16] superconductors with the $T_c$ higher than 77 K (liquid Nitrogen) are discovered. HgBaCaCuO show the highest $T_c$ value of 135 K [17]. Meanwhile, some other compounds are detected with superconductivity in this period. Third stage is after 2000, there is no increase in $T_c$ of superconductivity, but different types of superconductors are discovered. In which, MgB$_2$ found in 2001 [18] and Fe-based superconductors found in 2008 [19] are most attractive.

![Fig. 1-1 Brief history of discovery of superconductors](image)

In about 100-years history of superconductor, five Nobel prizes have been awarded for the scientists: Heike Kamerlingh Onnes (Discovery of superconductivity, 1913), John Bardeen, Leon N. Cooper, and J. Robert Schrieffer (BCS theory, 1972), Brian D. Josephson (Josephson effect, 1973), Georg Bednorz and K. Alex Müller (Discovery of superconductivity in cuprate perovskite, 1987),
Alexei A. Abrikosov, Vitaly L. Ginzburg, and Anthony J. Leggett (type-II superconductor, 2003). Although there are a lot of new superconductors are being discovered, the mechanism of superconductivity is still unclear, meanwhile the superconductor with high $T_c$ (such as room temperature) are still the dream for human beings. But superconductors have begun to be widely applied because of its special properties.

1.1.2 Superconducting properties and applications

Application is the goal of the research for any materials including superconductor. The properties of superconductor decide its applications. In this section, I will first introduce the basic superconducting properties, and then introduce the application of superconductors. As introduced in the 1.1.1, most superconductors used for practical applications are type-II superconductors, due to their high upper critical fields. So the discussions below are focused on type-II superconductors.

Fig. 1-2 shows the most important properties of superconducting materials. The relations among $T_c$, critical magnetic field ($H_c$ for type-II superconductor this is upper critical magnetic field, $H_{c2}$), and critical current density ($J_c$), are shown in Fig. 1-2. The surface in this three dimensional figure is the critical interface between the superconducting state and normal state. Inside the surface is the superconducting state, while outside is the normal state. The key properties of superconducting wires are their $T_c$, $H_{c2}$, $J_c$. $T_c$ and $H_{c2}$ are intrinsic properties of superconductors, and their values for superconducting wires are almost determined by the type of superconducting material used. In contrast, $J_c$ is an extrinsic property, and mainly depends on the microstructure of the superconductor. Therefore, the research on superconducting wires should be focused on the enhancement of $J_c$ by controlling the microstructure.
Superconductors are mainly used in the following fields:

1. **Superconducting magnets**: The superconducting magnets are mainly used in MRI, NMR, and the beam-steering magnets (used in particle accelerators). They can also be used for magnetic separation, such as in the environment and pigment industries.

2. **Electric applications**: such as power storage devices (SMES), transformers, electric motors, magnetic levitation devices (e.g. maglev trains), fault current limiters and power cables. However, superconductivity is sensitive to changing magnetic fields, so applications that use alternating current (e.g. transformers) will be more difficult to develop than those that use direct current.

3. **Superconducting quantum interference device (SQUID)**: superconductor is used to build Josephson junction which is the essential element of SQUID. SQUID is the most sensitive magnetometer to date.

4. **Superconducting device**: superconductors were used to build experimental digital computers using cryotron switches. They are also used to make digital circuits based on rapid single flux quantum technology and RF and microwave filters for mobile phone base stations.

### 1.1.3 Superconducting materials

Table. 1-1 summarizes the important superconducting material for the development of superconducting wires [20]. Their $T_c$ and $H_{c2}$ are also listed for comparison. The most widely used superconducting materials are Nb-Ti and Nb$_3$Sn. They are metallic superconductors, and are also low temperature superconductors (LTS). Nb-Ti is relatively easy to fabricate in superconducting wires, and occupies most of the low field magnets such as in MRI. Nb$_3$Sn is used for high field magnets. Both Nb-Ti and Nb$_3$Sn based magnets require liquid helium (LHe) as the coolant due to the low $T_c$, so their operating cost is expensive. High-temperature superconductors (HTS) with $T_c$ exceeding 77K have been widely studied since their discovery. Among them, Bi- and Y-based oxides are used for the development of superconducting wires cooled in liquid nitrogen which is much cheaper than LHe. But the HTS have many technical problems in making wires and coils. They have high anisotropy and only highly textured conductors have desirable performance. That is why the present HTS based magnets are mostly applied in low temperature. Fe-based superconductors have been attracting scientists since its discovery [19] because they contain ferromagnetic element, Fe, as a constituent. Some groups have reached good critical current properties with wires and tapes [21-23]. The $J_c$ dependence on magnetic field is very small which suggests that it is promising to be used for high field magnet. However, the toxic element arsenic may limit its practical applications.
Since its discovery in 2001 [18], MgB₂ with a transition temperature \( T_c \) at 39 K is expected to be used in liquid-helium-free conditions to replace metallic superconductors that are operated in a liquid helium environment. In contrast to high-\( T_c \) oxide superconductors, MgB₂ exhibits fairly strong grain coupling, indicating that grain alignment is not essential for obtaining high superconducting transport currents. This is a big advantage because the MgB₂ wires can be fabricated using a simple low-cost process. Furthermore, the abundant, low-weight, and environment-friendly raw materials that are used are special advantages compared to all other superconducting materials. Based on these advantages, MgB₂ appears to be an excellent candidate as a low-cost superconductor for large-scale applications. However, the critical current property of present MgB₂ wires is still low and needs to be enhanced for large-scale applications.

Table 1-1 Important superconducting materials for the development of superconducting wires

<table>
<thead>
<tr>
<th>Superconducting material</th>
<th>( T_c ) (K)</th>
<th>( H_{c2} ) at 4.2 K (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide superconductor (HTS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YBa₂Cu₃O₆⁺δ</td>
<td>92</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Bi₂Sr₂CaCu₂Oₓ</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Bi₂Sr₂Ca₂Cu₃Oₓ</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Tl₂Ba₂Ca₂Cu₃Oₓ</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>HgBa₂Ca₂Cu₂O₆</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>Metallic superconductor (LTS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb–Ti</td>
<td>9.8</td>
<td>11.5</td>
</tr>
<tr>
<td>Nb–Zr</td>
<td>10.5</td>
<td>11</td>
</tr>
<tr>
<td>V₃Ga</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>NbₓSn</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td>NbₓAl</td>
<td>18</td>
<td>32</td>
</tr>
<tr>
<td>Nbₓ(Al,Ge)</td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td>NbₓGa</td>
<td>20</td>
<td>34</td>
</tr>
<tr>
<td>NbₓGe</td>
<td>23</td>
<td>37</td>
</tr>
<tr>
<td>V₃(Al,Zr)</td>
<td>10.1</td>
<td>23</td>
</tr>
<tr>
<td>NbCN</td>
<td>17.8</td>
<td>12</td>
</tr>
<tr>
<td>MgB₂</td>
<td>39</td>
<td>25</td>
</tr>
<tr>
<td>Fe-based superconductor (LTS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SmFeAsO₁₋ₓFx</td>
<td>55</td>
<td>&gt;100</td>
</tr>
<tr>
<td>(Ba₁₋ₓKₓ)Fe₂As₂</td>
<td>38</td>
<td>70</td>
</tr>
</tbody>
</table>
1.2 MgB₂

1.2.1 Characteristics of MgB₂ superconductor

MgB₂ has a hexagonal crystal structure as shown in Fig. 1-3 [24]. The boron atoms form graphite-like honeycomb network and the Mg atoms are located at the pores of these hexagons. The in-plane B–B distance is almost half the inter-plane B–B distance. The Mg atom donates its valence electrons to the boron planes, which form ionic bonds with the boron atoms. The mechanism of superconductivity in MgB₂ was widely studied [25-27]. Eisterer M summarized it as [27]: Two three-dimensional (3D) metallic π-bands arise from the boron P, orbits. One band is electron type, and the other is hole type. Two σ-bands formed by the covalent p_xy orbitals which are deep beneath the Fermi energy in graphite cross the Fermi level in MgB₂. Charge is transferred from the σ- to the π-bands and holes are introduced in the σ-bands. The σ-bands retain their covalent character which is a peculiar feature of MgB₂. While the charge carriers of the π-bands are delocalized over the whole crystal, the σ-band holes are localized within the boron layers and the σ-bands are two dimensional (2D). The holes in the σ-bands strongly couple to the optical E₂g phonons (in plane boron bond stretching mode), which is mainly responsible for superconductivity in MgB₂. The π-band charge carriers become superconducting, too, although with significantly smaller energy gap, 2 meV. While energy gap of σ-bands is 7 meV.

MgB₂ is a brittle ceramics like the HTS materials. The anisotropy of MgB₂ (1.5~5) is lower than that of HTS [28], which suggests no grain orientation is needed for wire fabrication. This is in contrast to HTS. The coherence length of MgB₂ is 4–5 nm and the penetration depth is 100–140 nm at absolute zero kelvin [29]. Due to the large coherence length, larger than the interatomic spacing, the weak link problem is not severe in MgB₂. MgB₂ has a very sharp T_c-onset of 39–40 K and has a very narrow transition width of less than 1 K. The isotopic B¹⁰ substitution slightly increases the T_c-onset to 40.25 K [30]. Most of the element substitutions in MgB₂ resulted in a decrease of T_c.
1.2.2 MgB$_2$ superconducting wires

Mostly it is necessary to fabricate wire for applications of superconducting material. The most important property of superconducting wires for practical application is current transport ability (critical current density, $J_c$) in magnetic field. $J_c$ is divided critical current ($I_c$) by MgB$_2$ cross sectional area. Engineering $J_c$ ($J_e$) which is divided $I_c$ by the whole cross sectional area of wire, is more important for practical applications. The critical current properties ($J_c$ and $J_e$) of superconducting wires are governed by their microstructure and composition.

Some companies (Hype tech in USA [31], Columbus in Italy [32], and Hitachi in Japan [33]) have produced MgB$_2$ wires for products. The applications using MgB$_2$ such as MRI [34], SMES [35], and liquid H$_2$ level sensor [36] were studied at some labs in the world. Because the critical current properties of present MgB$_2$ wires are still low, most of these applications are considered in low field and low temperature such as 10-20 K. These temperatures can be obtained under liquid-helium-free condition using cryocooler. As introduced above, low cost is the most important advantage of MgB$_2$ wires. For large-scale practical applications, the critical current properties should be improved to save the operating cost (no helium). In order to meet these requirements of application, the critical current properties in 20 K (liquid hydrogen) and a high magnetic field of around 5 T should be enhanced.

Currently, powder in tube (PIT) process shown in Fig. 1-4 is the most popular method for the fabrication of MgB$_2$ wires. The starting powders were first packed into a tube, and then the tube was groove-rolled and drawn into a wire with demand diameter, finally the obtained wire was heat treated in a furnace to form MgB$_2$ wires.

![Fig. 1-4 Fabrication of MgB$_2$ wires with PIT process](image)
PIT process was divided into two categories with respect to the starting powder. MgB$_2$ powder is used for *ex situ* PIT [37-40], while mixture of Mg powder and B powder for *in situ* PIT [41-47].

The advantage of *ex situ* PIT process is that we can easily obtain high density MgB$_2$ core. However, we need high temperature heat treatment (higher than 900 °C) to obtain good connectivity of MgB$_2$ grains. Furthermore, impurity addition is not so easy as *in situ* method.

The *in situ* PIT process is widely used for the fabrication of MgB$_2$ wires. However, the reaction between Mg and B to form MgB$_2$ causes the volume-shrink (thus voids formation) in MgB$_2$ layer, resulting in the low density MgB$_2$ core. This low density MgB$_2$ core obtained by *in situ* PIT process leads to its low $J_c$ [48, 49]. Some methods such as mixing powders [50], high pressure [51], cold pressure [52] and hot pressing [53], are reported to increase the MgB$_2$ packing density and to enhance the $J_c$ values. Yamada *et al* [53] obtained high $J_c$ of 4.5 x 10$^4$ A/cm$^2$ at 10 T and 4.2 K by hot pressing. However, these methods increase the cost of the wire fabrication.

**1.2.3 Internal Mg diffusion process**

If we separate Mg and B (that is Mg diffuse to B layer from a separated place) to form MgB$_2$, we can decrease the voids in MgB$_2$ layer. Giunchi *et al* [54-56] first used an Mg diffusion method, and decreased the void formation problem effectively. They used a steel pipe as outer sheath, and Nb tube as an inner tube, in which a coaxial internal Mg rod and B powder was filled, to fabricate mono-filamentary and 7-filamentary wires. During the heat treatment, Mg (from the Mg rod) diffused to the B layer and reacted with B to form high density MgB$_2$ layer.

Our group has been studying this method and we have termed it as internal Mg diffusion (IMD) process. This process is shown in Fig. 1-5. An Mg rod was inserted into the center of a metal tube. Amorphous B powders (sometimes with additive) were packed into the space between the Mg rod and the tube. The composite billet was then cold worked to a wire by groove rolling and drawing, and then the wire was heat treated.

Fig. 1-5 Fabrication of MgB$_2$ wires by IMD process
Fig. 1-6(a) and (b) show typical transverse and longitudinal cross sections of IMD-processed wire before heat treatment observed by an optical microscopy, respectively. The cross sections show uniform deformation of the composite. As we know, pure Mg has poor deformability at room temperature. However, the existence of B powder surrounding Mg rod improves the deformability of pure Mg rod. Fig. 1-6(c) and (d) show transverse and longitudinal cross section of IMD-processed MgB$_2$ wire after heat treatment, respectively. MgB$_2$ layer is formed uniformly along the Fe inner wall and at the center a large hole is generated. Increase of the MgB$_2$ area fraction, both by decreasing of the hole in wire center and decreasing the sheath area, can increase the engineering critical current density ($J_e$) of IMD-processed MgB$_2$ wires.

![Optical Microscopy Images](image1.png)

Fig. 1-6 Typical optical microscopy of cross sectional images of IMD-processed MgB$_2$ wire with diameter of 1.2 mm by optical microscopy, (a) transverse and (b) longitudinal cross section before heat treatment, (c) transverse and (d) longitudinal cross section after heat treatment

Fig. 1-7 shows several IMD-processed MgB$_2$ wires. Uniform MgB$_2$ layers are observed along the inner wall of Fe sheath for all wires, which suggests that the IMD process can be used to fabricate large-scale MgB$_2$ wires with uniform MgB$_2$ layer.
Fig. 1-7 The uniformity in longitudinal direction of the several IMD-processed MgB2 wires

Fig. 1-8 (a) and (b) show the typical SEM images of the MgB2 layer of IMD and PIT-processed MgB2 wires, respectively. The MgB2 layer of IMD-processed wire is dense while the MgB2 layer of PIT-processed wire contains many voids and impurities. But the IMD-processed MgB2 layers have many uneven black spots which are the un-reacted boron or the boron-rich phase as discussed in chapters 2-4.

Fig. 1-8 Typical SEM image of MgB2 wires (a) IMD processed MgB2 wires, (b) PIT processed MgB2 wires
1.3 Thesis content

1.3.1 Research purpose, theory, and research methods

The title of this thesis is “the development of high performance MgB₂ wires”. Low cost is the most important advantage of MgB₂ to be used as a practical superconducting wire. The purpose of this research is to develop MgB₂ superconducting wires for practical applications with low cost. Currently, there have already been products using MgB₂ superconductors, but the cost of these products are not so low because the critical current properties of these MgB₂ wires are not high enough to operate in the expected condition. The expected condition for MgB₂ wire operation is the operation at ~20 K using a cryocooler or liquid hydrogen. Considering the industrial applications of MgB₂ wires, the \( J_c \) of \( 1.0 \times 10^5 \) A/cm² and \( J_e \) of \( 2 \times 10^4 \) A/cm² at 20 K and 5 T should be the target values of MgB₂ wire development. Thus the main task of my study is to enhance the critical current properties for MgB₂ wires at 20 K and 5 T. However, I mostly studied the \( J_c \) and \( J_e \) value at 4.2 K and 10 T, because \( I_c \) can be more easily measured under this condition than those at 20 K and 5 T. Although there seems to be no liner relations between the 4.2K^10T and 20K^5T, I select the good samples referring to \( I_c \) at 4.2K^10T for the \( I_c \) measurement at 20K^5T.

Collings E W et al. [57] summarized how to improve the critical current properties of MgB₂ superconducting wires. They considered that there are mainly four factors which determine the critical current properties of MgB₂ wires.

(a) The \( H_{c2} \): The \( H_{c2} \) of MgB₂ can be enhanced by dopant. Many effective dopants have been reported for MgB₂. Among them, only C-containing materials have turned out to be the most promising. Carbon atoms substituted for B site produce strong impurity scattering in the \( \pi \) band (as well as the \( \sigma \) band), which is responsible for the increase of \( H_{c2} \). There are many C-containing materials, such as elemental C, C-containing inorganic and organic compounds. The most popular dopant is SiC.

(b) Flux pinning: Some kinds of impurities are effective flux pinning centers. But the main flux pinning center in MgB₂ is flux pinning at grain boundaries. Therefore, small grain size increases the flux pinning at grain boundaries. Impurities also affect the flux pinning at grain boundaries because some impurities can prevent the grain growth, resulting in a small grain size.

(c) Connectivity: Sometimes insulating MgO or amorphous BOₓ layers were observed at MgB₂ grain boundaries. These layers are obstacles of superconducting current. Anisotropy has also influence on grain-to-grain current flow in untextured polycrystalline materials, so it is also addressed as a factor affecting connectivity.
(d) Porosity: Porosity (and also voids) is commonly observed in PIT-processed MgB$_2$ wires, especially, in situ PIT-processed wires. The reduction of porosity is very important to increase $J_c$ of MgB$_2$ wires.

Taking into account of the factors summarized by Collings E W et al. [57] and research situation when I started the work, I designed my methods to study the MgB$_2$ wires as follows:

1. I selected IMD process for fabricating MgB$_2$ wires because the PIT process has the voids (porosity) problem for both ex situ and in situ PIT processes. Furthermore, IMD process improves the connectivity by decreasing MgO. Compared to Mg powder used for PIT process, the Mg rod used for IMD process contains less amount of MgO.

2. $J_c$ increases with increasing the MgB$_2$ area fraction for IMD-processed MgB$_2$ wires. Decrease in hole of the wire center and decrease of sheath area can both increase the MgB$_2$ area fraction.

3. $J_c$ increases by the improvement of the reaction between Mg and B for IMD-processed MgB$_2$ wires. Decrease in un-reacted B particles and decrease in B-rich region can be both obtained by the improvement of the reaction between Mg and B.

4. Multi-filamentary IMD-processed MgB$_2$ wires are developed. The multi-filamentary IMD wires decrease the MgB$_2$ filament size, resulting in decrease of the Mg diffusion distance, which can improve reaction between Mg and B. Furthermore, the multi-filamentary MgB$_2$ wires show good stability which is suitable for practical applications.

5. Carbon-containing material addition is effective to improve $J_c$ values for the IMD-processed MgB$_2$ wires as well as PIT-processed MgB$_2$ wires. Our group has already obtained good results by applying SiC addition to IMD MgB$_2$ wires. However, the uniform dispersion of additive is very important. It is not easy to obtain a uniform mixture of solid SiC and solid B powders. Hence I tried to add a liquid aromatic hydrocarbon to obtain a uniform mixture of SiC and B powders. This is my original consideration though other groups also used the liquid aromatic hydrocarbon for PIT-processed wires. Furthermore, the liquid aromatic hydrocarbon can be absorbed on the surface of B powder, which can (1) increase the amount of carbon substitution for B (increase $H_c$), and (2) prevent the MgB$_2$ grain growth (increase flux pinning at grain boundaries), thus enhancement of $J_c$.

6. Organics addition, especially aromatic hydrocarbon addition, is searched to improve $J_c$ values. The aromatic hydrocarbons have only carbon and hydrogen in molecule, and they have the highest carbon content in all organics; hence they take less impurity (such as oxide) to MgB$_2$ wire. Furthermore, they are more stable than other elemental carbon such as carbon nano particles. Compared to the inorganics, the low boiling point and decomposing temperature make them easy to obtain the uniform fresh carbon. This fresh carbon can both substitute for B and work as pinning center. My chemistry knowledge is also useful to search the ideal aromatic hydrocarbon.
7. A new inorganic additive without carbon is searched to improve $J_c$ values. Carbon substitution for B enhances $J_c$ only in high magnetic field. However, $J_c$ in low field decreases because carbon decreases the connectivity of MgB$_2$ grains. A new additive is expected to increase $J_c$ in both high field and low fields.

8. The B powder was refined. Chemistry solvent is expected to remove the impurities absorbed on the surface of B powders.

The details of my research plan are introduced in 1.3.3. I selected the IMD process for my Ph.D work as described in 1. In order to deal with 2 and 3, I tried to add Mg powder to B layer of IMD-processed MgB$_2$ wire, and then developed a new method by a combination of IMD and PIT. These works are introduced in chapter 2. The 4 is introduced in chapter 3, the fabrication of IMD-processed 37-filamentary MgB$_2$ wire was first successfully carried out. The 5 is carried out in chapter 4, SiC and liquid aromatic hydrocarbon co-addition is introduced. The 6, organics addition, is carried out in chapter 6. This work is to replace the carbon-coated nano-sized B powder introduced in chapter 5. A lot of materials are tried for the 7. I don’t describe them in this thesis because they are mostly failed. Chapter 5 and 6 can also be considered as examples for refining B powder described in the 8.

1.3.2 The characterization methods

The low transport critical current properties are the bottleneck for the development of high performance MgB$_2$ wires for large-scale practical applications with low cost. In this study, I mainly estimated the critical current properties for MgB$_2$ wires. The value of $J_c$ for each wire was calculated by dividing transport critical current ($I_c$) by the whole cross sectional area of MgB$_2$ layer including B-rich region. Furthermore, the engineering $J_c$ ($J_c^{e}$) calculated by dividing $I_c$ by the entire wire area in the transverse cross section was also estimated. The $I_c$ values for the wire were measured at temperatures of 4.2, 10, 15, 20, 25, and 30 K in magnetic fields below 18 T using a four-probe resistance method. The two current probes were soldered to either end of a 4-cm-long wire and the two voltage probes were soldered to the middle of the wire, with a spacing of 1 cm between them. $I_c$ was defined as a voltage drop of 1 $\mu$V across the voltage probes.

The microstructures were observed by the optical microscope (OM), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and scanning TEM (STEM). Structural analyses were carried out with X-ray diffraction (XRD) analysis, Energy dispersive X-ray spectroscopy (EDX), and Electron energy loss spectroscopy (EELS).
1.3.3 The research experience and thesis structure

In 2008, Hur et al. [58] fabricated the IMD-processed MgB$_2$ wires with SiC-added B powder (99.99%, 300-mesh, Sigma-Aldrich Co.), and obtained a much improved $J_c$ of $4.1 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T. Then Togano et al. [59, 60] and Kumakura et al. [61] fabricated multi-filamentary (7 and 19 filaments) IMD wires. Their $J_c$ values for the MgB$_2$ layer achieved as high as $1 \times 10^5$ A/cm$^2$ at 4.2 K and 10 T. As introduced above, these high $J_c$ values are mostly due to the high density MgB$_2$ layer produced by IMD process.

In 2007, Yamada et al. [62] reported that the SiC and ethyltoluene co-added MgB$_2$ wire showed higher $J_c$ than the only SiC-added wire.

Accordingly, I started my work by applying the SiC and ethyltoluene co-addition to IMD-processed MgB$_2$ wire. Co-addition of SiC and toluene, and SiC and dimethylbenzene were also tried to IMD MgB$_2$ wires. And I found that they were more effective than SiC and ethyltoluene co-addition [63]. Through the observation of microstructure, I found that the un-reacted B particles exist in IMD MgB$_2$ wires [64]. In order to decrease the un-reacted B particles, I added Mg powder to B layer of IMD MgB$_2$ wires and developed a new method which combined IMD and PIT processes for MgB$_2$ wire fabrication. This new method increase $J_c$ of MgB$_2$ wires by increasing MgB$_2$ area fraction. We also found that using carbon-coated nano-sized B powder to replace the SiC addition can obtain high $J_c$ values with less un-reacted B particles. Thus, I mainly separated my Ph.D thesis in two parts. The first part is the fabrication of MgB$_2$ wire. The new method combining IMD and PIT processes (chapter 2) and 37-filamentary IMD-processed MgB$_2$ wires (chapter 3) were described. The second part is impurity addition. The SiC and liquid aromatic hydrocarbon co-addition to 325-mesh B powder (chapter 4), nano-sized B powder with C-coating (chapter 5), and nano-sized B powder with coronene addition (chapter 6) were described.

In chapter 2, I tried to add Mg powder to IMD-processed MgB$_2$ wires and decreased the un-reacted B particles [65]. The mechanism of decreasing the un-reacted B particles by the Mg powder addition is considered to be that the added Mg power decreases the required Mg diffusion distance and improves the reaction between Mg and B. However, the Mg powder addition also caused void formation as in the case of PIT process. These voids decrease the $J_c$ values. I found that the $J_c$ and $J_e$ are influenced by the un-reacted B particles and the voids. If I continue to add the Mg powder in B layer of IMD-processed MgB$_2$ wires, the Mg rod should be decreased to make a balance between Mg and B. Based on this consideration, a new method which combined IMD and PIT processes is developed [66]. By this new method, the hole in the center of IMD-processed MgB$_2$ wires can be decreased, simultaneously the thickness of MgB$_2$ layer can be increased. Both decrease of hole and increase of MgB$_2$ layer thickness cause the increase of MgB$_2$ area fraction, thus increase the $J_c$ of IMD-processed MgB$_2$ wires [58-61].
In chapter 3, I successfully fabricated 37-filamentary IMD-processed MgB$_2$ wires [67]. The critical current properties, microstructure, and impurity addition were investigated. The filament size of as small as 100 μm was realized in the IMD-processed MgB$_2$ wires. Furthermore, this study directly proved that the short B layer thickness can decrease the amount of un-reacted B particles. The successful fabrication of 37-filamentary wire suggests that IMD process can be used to fabricate the long MgB$_2$ wires for large-scale practical applications.

In chapter 4, SiC and liquid aromatic hydrocarbon co-addition to IMD-processed MgB$_2$ wires fabricated with low quality B powders (325-mesh, 99%) was described. As introduced above, this works is not only the starting point, but also the jointing point of two parts in my Ph.D thesis as introduced above.

All the works in chapters 2-4 were carried out with the low quality B powders (325-mesh, 99%). It was difficult to import high quality amorphous B powder because it can be used to produce the weapon. When I was doing the work introduced in chapters 2-4, the Ohio state university and hyper tech company used a special plasma-synthesized carbon-coated B powder (Special Materials Inc., SMI powder) to fabricate thin IMD-processed MgB$_2$ wires (diameter: 0.55 mm) with Nb and Monel double sheaths, and they obtained a high $J_c$ and $J_e$ values for IMD processed MgB$_2$ wires [68]. I also got this B powders, but I found it was difficult to obtain the high critical current as theirs if I don’t apply pre-treatment to the B powder. This leads to the work below.

In chapter 5, I pretreated the C-coated nano-sized B powder by dimethylbenzene and fabricated the IMD-processed MgB$_2$ wires. The higher critical current properties than those of Ohio state university were obtained [69, 70]. The dimethylbenzene decreases Cl in the B powders, which is the main reason for higher $J_c$. I obtained. Ohio state university recently reported a higher $J_c$ value at 4.2 K and 10 T in their paper [71]. However, there are arguments because they calculated the $J_c$ by MgB$_2$ area without the B-rich region. In fact, there is MgB$_2$ in the B-rich region who transports the superconducting current.

Although the high critical current densities were obtained from the SMI B powder, my experiments showed that this B powder is unstable [69, 70]. In addition, this B powder is expensive due to its complex synthesis process [72]. I changed this B powder for another B powder which is discussed in chapter 6.

In chapter 6, we used a new B powder, which is also nano-sized, but undoped B powder. I added an aromatic hydrocarbon (coronene, C$_{24}$H$_{12}$) to this new B powder and fabricated IMD-processed MgB$_2$ wires with a diameter of 0.6 mm. I obtained the same level critical current properties as the SMI B powders [68-71]. The B powder without carbon-coating is much stable and cheap, which are due to its simple synthesis process. The C$_{24}$H$_{12}$ is a popular organic material with no toxicity. The result in chapter 6 is expected to be used in the practical level long wire fabrication.
In addition, Chapter 1 introduced the background and contents of this thesis. In chapter 7, firstly the thesis was summarized. Then some on-going works are introduced. Finally, the future works are proposed.

Reference

[1] Onnes Kamerling H 1911 Leiden Comm. 120b, 122b, 124c
[12] Zhang Y H 2008 ChaoDaoWuLi ISBN 978-7-312-02177-0
[34] http://www.columbussuperconductors.com/
[36] http://www.lib.kobe-u.ac.jp/repository/81003939.pdf#search= 'MgB2+%E6%B6%82%E9%9D%A2 %E8%A8%88'
[38] Braccini V, Nardelli D, Penco R and Grasso G 2007 Physica C 456 209
[73] Ye et al. Preparation
Chapter 2 Development of a new method combining IMD and PIT processes for MgB₂ wires

2.1 Introduction

As introduced in chapter 1, we found that the un-reacted B particles exist in the MgB₂ layer which decreases the \( J_c \) properties. The un-reacted B particles are considered to be caused by an insufficient reaction between Mg and B layer due to the long diffusion distance of Mg atoms. These un-reacted B particles are non-superconducting phase, hence, decrease the \( J_c \) properties. Here, I explored a new approach - Mg powder addition to the B layer of IMD-processed MgB₂ wires in order to reduce the un-reacted B particles by decreasing the average Mg diffusion distance. Our results showed that this is an effective method to decrease the un-reacted B particles [1]. But it also produced the voids in the MgB₂ layer which is caused by the volume shrink as in the case of PIT process.

If I continue to increase the amount of Mg powder addition to the B layer, the Mg rod diameter should simultaneously be decreased to balance the ratio of Mg and B (1 : 2) to form MgB₂. In the case of 50 mol% Mg powder addition (stoichiometric composition), the diameter of the Mg rod needs to be decreased to 0, which means the IMD process (schematically shown in Fig. 2-1 (a)) changes to the PIT process (schematically shown in Fig. 2-1 (b)). The process with Mg powder addition lower than 50 mol% Mg is in fact a combination of IMD and PIT processes [2] (Schematically shown in Fig. 2-1 (c)).

![Fig. 2-1 Schematic maps of the transverse cross sections for MgB₂ wires fabricated with (a) IMD, (b) PIT, and (c) a new method combining IMD and PIT](image-url)
In this chapter, I will introduce this new method of hybridization of IMD and PIT processes for MgB$_2$ wires by two steps: Firstly, small amounts of Mg powder is added to B layer of IMD-processed MgB$_2$ wires without the change of Mg rod diameter, and secondly, Mg powder addition to B layer of IMD-processed MgB$_2$ wires is increased and Mg rod diameter is decreased. The first step focuses on the IMD process with Mg powder addition. The second step mainly introduces a new method which is a hybrid method of IMD and PIT processes. The details for this chapter are described in my previous paper [1, 2].

2.2 Enhancement of critical current properties of IMD-processed MgB$_2$ wires by Mg addition

2.2.1 Experimental details

An Mg rod (diameter: 2.0 mm) was polished with abrasive paper to remove the oxide and then put into the center of an Fe tube (inner diameter 3.5 mm, outer diameter 6.0 mm). A mixture of amorphous B powder (99%, 325-mesh) and Mg powder (99.8%, 325-mesh) prepared by grinding in an agate mortar was packed into the space between the Mg rod and the Fe tube. The concentration of the Mg in the mixture was varied as 0 mol%, 3 mol%, 6 mol%, 9 mol% and 12 mol%. The composite billet was then cold worked (by groove rolling, swaging, and drawing) to a wire with a diameter of 1.16 mm. After the cold working, short samples of 40 mm length were cut from the wire and subjected to heat treatment. We also prepared wires in which nano-sized SiC powder was added together with the Mg powder to B powder, with the fixed (10 mol%) concentration of SiC. Undoped PIT-processed mono-core wire from the same B and Mg powders with diameter of 1.0 mm was fabricated for comparison. The specifications of wires fabricated in this study are listed in table 2-1.

Table 2-1. The specifications of all MgB$_2$ wires

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Doped SiC (mol%)</th>
<th>Doped Mg powder (Mg/total, mol%)</th>
<th>Diameter (mm)</th>
<th>Slope of $I_s$ vs $I$ (S/I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Pure, IMD</td>
<td>0</td>
<td>0</td>
<td>1.16</td>
<td>-0.358</td>
</tr>
<tr>
<td>A2</td>
<td>3 mol% Mg, IMD</td>
<td>0</td>
<td>3</td>
<td>1.14</td>
<td>-0.337</td>
</tr>
<tr>
<td>A3</td>
<td>6 mol% Mg, IMD</td>
<td>0</td>
<td>6</td>
<td>1.16</td>
<td>-0.345</td>
</tr>
<tr>
<td>A4</td>
<td>9 mol% Mg, IMD</td>
<td>0</td>
<td>9</td>
<td>1.16</td>
<td>-0.346</td>
</tr>
<tr>
<td>A5</td>
<td>12 mol% Mg, IMD</td>
<td>0</td>
<td>12</td>
<td>1.16</td>
<td>-0.328</td>
</tr>
<tr>
<td>B</td>
<td>pure, PIT</td>
<td>0</td>
<td>33.3</td>
<td>1.0</td>
<td>-0.364</td>
</tr>
<tr>
<td>C1</td>
<td>10 mol% SiC, IMD</td>
<td>10</td>
<td>0</td>
<td>1.16</td>
<td>-0.204</td>
</tr>
<tr>
<td>C2</td>
<td>10 mol% SiC + 3 mol% Mg, IMD</td>
<td>10</td>
<td>3</td>
<td>1.16</td>
<td>-0.203</td>
</tr>
<tr>
<td>C3</td>
<td>10 mol% SiC + 6 mol% Mg, IMD</td>
<td>10</td>
<td>6</td>
<td>1.16</td>
<td>-0.199</td>
</tr>
<tr>
<td>C4</td>
<td>10 mol% SiC + 9 mol% Mg, IMD</td>
<td>10</td>
<td>9</td>
<td>1.16</td>
<td>-0.201</td>
</tr>
</tbody>
</table>
All samples (40 mm length) with no seal at the ends were wrapped with Zr foils and were heated in a furnace as the following process: We first raised the temperature from room temperature to 640 °C in 1 hour, then raised it gradually to 670 °C in 3 hours, held this temperature for 2 hours, and finally cooled the specimens to room temperature in the furnace. This slow raising temperature from 640 °C (lower than Mg melting point, 650 °C) was applied to make the Mg diffuse into B layer rather than vaporize. The heat treatment was carried out in an Ar gas atmosphere (1 atm).

The transport critical current ($I_c$) of the wires was measured using the four-point resistive method. The $I_c$ was calculated for the cross-sectional area of the reacted layer. While the $I_c$ for the cross-sectional area of the whole wire was also calculated. The cross section of the wire was observed using optical microscopes (KEYENCE VK-8500 for low magnification, while OLYMPUS BX60M for high magnification). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out with the Hitachi SU-70 and JEM-2100F, respectively. The sample for TEM was a film with a thickness of 100 nm which was taken from the transverse cross section of a wire and thinned using a focused ion beam (JEOL JEM-FIB9320). STEM dark field (STEM-DF) observations were carried out with a camera length of 20 cm and a collection angle ranging from 70 to 184 mrad.

### 2.2.2 Results and discussion

Fig. 2-2(a) and (b) show the $I_c$-$B$ curves and $I_c$-$T$ curves at 4.2 K for the IMD-processed MgB$_2$ wires, respectively. Undoped and Mg-added wires are compared. We only measured $I_c$ in fields higher than 6 T because $I_c$ below 6 T was sufficiently high to quench and deteriorates the wires due to the resulting increase in temperature. The value of $I_c$ increased with increasing Mg concentration, with a maximum value at 6 mol% Mg addition; $I_c$ then decreased for higher Mg concentrations. The slopes of $I_c$-$B$ curves in Fig. 2-2(a) defined with the field range of 10-12 T were shown in table 2-1. All the wires showed almost the same slopes indicating that the magnetic field dependence of $I_c$ was not changed. We ascribe the reduction of $I_c$ at Mg concentrations over 6% to the volume shrinkage (leading to porosity) caused by the reaction between the Mg powder and the B powder, which is well known in the PIT process. The $I_c$ of the 6 mol% Mg-added MgB$_2$ wire was about twice as high as that of the undoped wire, and is about $1.2 \times 10^4$ A/cm$^2$ in 4.2 K and 10 T. $I_c$ shows similar behavior to $J_c$. Both $J_c$ and $I_c$ values show that the addition of Mg powder to B layer is an effective method to decrease the un-reacted B particles in IMD MgB$_2$ layer, and thus enhances critical current properties of IMD-processed MgB$_2$ wires.
Fig. 2-2 (a) $J_c$-$B$ curves and (b) $J_e$-$B$ curves of IMD-processed undoped and Mg-added MgB$_2$ wires
Fig. 2-3(a) and (b) show magnified optical microscope images of transverse cross section of undoped and 6 mol% Mg-added IMD-processed MgB$_2$ wires, respectively. Our previous results [3-5] indicated that the main phase of the reacted layer (yellow domain) is MgB$_2$, and the blue particles in the reacted layer are the un-reacted B particles. The black spots found in the Fe tube and reacted layer correspond to resins from the polishing process. Compared to the case of the undoped IMD wire shown in Fig. 2-3(a), the presence of unreacted particles decreased in the 6 mol% Mg-added wire as shown in Fig. 2-3(b). A high density of un-reacted B particles was observed at an area far from the hole in Fig. 2-3(a), which can be explained by the long Mg diffusion distance from the center of the wire. This result is consistent with the results of Shimada et al. [6]. Un-reacted B particles in the Mg-added wires in Fig. 2-3(b) can be explained by the fact that the starting B powders contained some large particles and these were not easily crushed using a mortar in our lab.

Fig. 2-3 Magnified optical microscope images of transverse cross-section of IMD-processed (a) undoped and (b) 6 mol% Mg-added MgB$_2$ wires

Fig. 2-4(a) and (b) show SEM images of longitudinal cross section of undoped and 6 mol% Mg-added IMD-processed MgB$_2$ wires, respectively. The 6 mol% Mg-added wire has smaller size and less amounts of un-reacted B particles than that of undoped wire in longitudinal cross-section, which is consistent with the transverse cross-section shown in Fig. 2-3(a) and (b). Some voids can also be found in the 6 mol% Mg-added IMD-processed MgB$_2$ wires, which was due to the volume shrinkage when added Mg powder reacted with B. These voids increase as the Mg powder addition increases.
The samples for TEM observations were taken from the transverse cross section of the wires where no un-reacted B layer was found by optical microscopy (yellow domain in Fig. 2-3(a) and (b)).

Fig. 2-5(a) shows a STEM-DF image of undoped samples prepared by the FIB. Fig. 2-5(b) shows a magnified STEM-DF image of the red frame in Fig. 2-5(a). There are two kinds of regions in Fig. 2-5(b), marked (A) and (B). Fig. 2-5(c) and (d) show the high resolution images of the (A) and (B) regions, respectively. Our previous research [7] showed that the region A is polycrystalline, consisting mainly of MgB$_2$ and MgO for the undoped wires, and MgB$_2$, MgO and Mg$_2$Si for the SiC-added wires. The fast Fourier transform (FFT) observed from the region of red frame in Fig. 2-5(c) shows that the crystal is MgB$_2$ grain, observed in [011] direction. Region B is the amorphous phase as shown in Fig. 2-5(d) and corresponds to un-reacted B particles for both undoped and SiC-added wires.
Fig. 2-5 (a) STEM dark field (DF) image of the reacted layer in undoped MgB$_2$ wire. (b) Magnified STEM-DF image of the red frame in Fig 2-4(a). (c) High resolution image of region (A) in Fig 2-4(b). (d) High resolution image of region (B) in Fig 2-4(b).

Fig. 2-6 shows a STEM-DF image of the 6 mol% Mg-added wire. Compared to the undoped wires shown in Fig. 2-5(a), there are no large amorphous regions in the Mg-added wires. As mentioned above, these samples were taken from the wires wherein un-reacted B particles could not be observed in the optical microscope. This indicates that Mg powder addition decreased the amount of un-reacted B particles even in TEM level. This is in contrast to the case of undoped wire shown in Fig. 2-5(a). Thus, the decrease in the Mg diffusion distance of IMD-processed MgB$_2$ wires by the Mg powder addition was effective in reducing the amount of un-reacted B particles. This decrease in the quantity of un-reacted B particles is likely responsible for the $J_c$ enhancement seen in Fig. 2-2.
The concentration of the Mg powder in the starting powders (mixture of Mg and B powders) of the PIT-processed MgB$_2$ is $\sim$33 mol%. Fig. 2-7 shows the $J_c$ value at 4.2 K and 10 T as a function of the Mg concentration in the B powders. $J_c$ increases with increasing Mg concentration due to the decrease in the amount of un-reacted B particles, while $J_c$ decreased above 6 mol% Mg concentration since the porosity in the reacted layer increased with increasing Mg concentration. Although the $J_c$ started to decrease slowly at the range of 9 ~ 12 mol% Mg addition, we speculate that $J_c$ will monotonically decrease if we increase the Mg concentration above 12 mol% and correspondingly decrease the diameter of the Mg rod at the center of the wire. Finally, at 33 mol% Mg concentration with no Mg rod present, the wire becomes a PIT-processed wire and we obtained low $J_c$ value of about $1.6 \times 10^3$ A/cm$^2$ at 4.2 K and 10 T.
Fig. 2-8 (a) $J_c$-$B$ and (b) $J_e$-$B$ curves of the IMD-processed MgB$_2$ wires with 10 mol% SiC addition and 10 mol% SiC and Mg powder (3, 6, and 9 mol%) co-addition
Fig. 2-8(a) and (b) show the $J_c$-$B$ curve and $J_e$-$B$ curve at 4.2 K for IMD-processed MgB$_2$ wires with 10 mol% SiC addition and 10 mol% SiC and Mg (of 3 mol%, 6 mol% and 9 mol%) co-addition, respectively. We only measured $I_c$ in fields higher than 8 T because $I_c$ below 8 T for all the wires is sufficiently high to quench and deteriorates the wires. The slopes of $J_c$-$B$ curves in Fig. 2-7(a) were shown in Table 2-1. All the slopes (absolute value) of the $J_c$-$B$ curves for SiC added wires are smaller than those of the wires with no SiC addition in Fig. 2-2 due to the C-substitution at the B sites. The slopes of the $J_c$-$B$ curves in Fig. 2-8(a) and (b) are all nearly the same, indicating that Mg addition did not further change the magnetic field dependence of $J_c$. Here, 6 mol% Mg powder and 10 mol% SiC co-added wire has the highest $J_c$ and $J_e$ values. While 6 mol% Mg powder added wire also shows the highest $J_c$ and $J_e$ values for wires without SiC addition. This suggests that the mechanism of $J_c$ enhancement by the Mg powder addition is the same for both undoped and SiC-added wires. $J_c$ for the 10 mol% SiC and 6 mol% Mg co-added wires was 1.2 times higher than that of only SiC-added wires in all measured magnetic fields. This $J_c$ increase is smaller than that for the wires with no SiC-added. The highest $J_c$ obtained in this experiments is about $5 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T, which is almost same with the high $J_c$ value we obtained using high quality B powder with SiC and toluene co-addition [8, 9].

Fig. 2-9 (a) and (b) show STEM-DF images of 10 mol% SiC-added wires and 10 mol% SiC and 6 mol% Mg co-added wires, respectively. SiC-added wires have un-reacted B particles marked as B, while there are less (almost no) un-reacted B particles in the co-added wire. This result is similar to that for the undoped wires and Mg-added wires, suggesting that Mg addition is an effective way to reduce the amount of un-reacted B particles and enhance $J_c$ in impurity-added IMD-processed MgB$_2$ wires.

![Fig. 2-9 STEM-DF images of (a) 10 mol% SiC-added (b) 10 mol% SiC and 6 mol% Mg powder co-added IMD-processed MgB$_2$ wires](image)
2.3 Fabrication of MgB₂ wires with a new method combining IMD and PIT processes

As introduced in 2.1, if we continue to increase the Mg powder addition to IMD-processed MgB₂ wires, we should decrease the Mg rod diameter to make a balance between Mg and B. This is a new method—a combination of IMD and PIT processes for MgB₂ wires. In this section, I will discuss this new method for the fabrication of MgB₂ wires.

2.3.1 Experimental details

A 2 mm diameter Mg rod was polished with abrasive paper to remove surface oxide and then put into the center of a Fe tube with a 6 mm outer diameter. A mixture of amorphous B powder (99 %, 325-mesh, Alfa Aesar), Mg powder (99.8%, 325-mesh, Alfa Aesar) and nano-sized SiC were prepared by grinding in an agate mortar which was packed into the space between the Mg rod and the Fe tube. The composite billet was then cold worked (by groove rolling and drawing) to a wire with a diameter as shown in Table 2-2. Details of the MgB₂ wire fabrication were described in our previous paper [1-5, 7-8]. The concentration of SiC to B powder was 10 mol% for all wires. Three wires were fabricated with the mixing process of IMD and PIT and were named M1, M2, and M3, respectively. The amount of Mg powders added into the B layer were 6 mol%, 17 mol%, and 25 mol% for the three wires. The Mg rod diameters were 2 mm, 1.7 mm, and 1.4 mm, and the Fe tube inner diameters were 3.5 mm, 4.0 mm, and 4.0 mm to keep the ratio of Mg to B the same as the IMD-processed MgB₂ wire. IMD-processed MgB₂ wires termed M0 and PIT-processed MgB₂ wires termed P0 were also fabricated. The specifications of all these wires are listed in Table 2-2. The heat treatment process for IMD-processed MgB₂ wires (4 cm length) is described in (2.2.1).

Table 2-2. Details of the fabricated wires

<table>
<thead>
<tr>
<th>No.</th>
<th>M0</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>P0</th>
</tr>
</thead>
<tbody>
<tr>
<td>State</td>
<td>IMD</td>
<td>IMD+PIT</td>
<td>IMD+PIT</td>
<td>IMD+PIT</td>
<td>PIT</td>
</tr>
<tr>
<td>Wire diameter (mm)</td>
<td>1.16</td>
<td>1.16</td>
<td>1.2</td>
<td>1.26</td>
<td>1.0</td>
</tr>
<tr>
<td>Mg rod (mm)</td>
<td>2</td>
<td>2</td>
<td>1.7</td>
<td>1.4</td>
<td>0</td>
</tr>
<tr>
<td>Mg rod area (mm²)</td>
<td>1.7</td>
<td>1.7</td>
<td>0.72</td>
<td>0.49</td>
<td>0</td>
</tr>
<tr>
<td>Fe inner diameter (mm)</td>
<td>3.5</td>
<td>3.5</td>
<td>4</td>
<td>4</td>
<td>3.5</td>
</tr>
<tr>
<td>Mg powder concentration (Mg : B, mol%)</td>
<td>0</td>
<td>6%</td>
<td>17%</td>
<td>25%</td>
<td>50%</td>
</tr>
<tr>
<td>MgB₂ area fraction (%)</td>
<td>8%</td>
<td>8.1%</td>
<td>21.4%</td>
<td>23.8%</td>
<td>25.3%</td>
</tr>
</tbody>
</table>
A 10 mol% SiC-added PIT mono-core wire with a diameter of 1.0 mm was fabricated from the same B and Mg powders for comparison. This PIT wires (4 cm length) were heated as follows: The temperature was raised to 850 °C for 1 hour, held for 1 hour, and then cooled down in the furnace. We used a higher heat treatment temperature than that for the IMD process because it can yield higher critical current properties for PIT MgB2 wires fabricated with the same starting materials.

Scanning electron microscopy (SEM) observations and energy dispersive X-ray spectrometry (EDS) mapping were carried out using a Hitachi SU-70 instrument. The cross-sectional area of the reacted layer was observed using an optical microscope (OM, KEYENCE VK-8500). The transport critical current ($I_c$) of the wires was measured using the four-probe resistive method. $I_c$ was calculated for the cross-sectional area of the reacted MgB2 layer, while $J_c$ was calculated for the cross-sectional area of the whole wire.

2.3.2 Results and discussion

Fig. 2-10(a) shows an optical microscope image on the transverse cross section of M0, which is the representative image for the IMD-processed MgB2 wire. The MgB2 layer is orange in color, due to the high density MgB2 layer reflecting light, which is consistent with the MgB2 crystal reported by Lee et al. [9]. Fig. 2-10(b) shows an image of P0, which is the representative image for the PIT-processed MgB2 wire. The MgB2 layer is dark, which is due to the large amount of voids in the PIT-processed MgB2 layer absorbing light. Fig. 2-10(c) shows an image of M2. The color in the reacted MgB2 layer is uniform, which indicates that the reaction is completed (no B-rich region) although the MgB2 thickness is large (almost 140 μm). As listed in table 2-2, the MgB2 area fraction for M2 and M3 are 21.4% and 23.8%, respectively. The reacted MgB2 area fraction of MgB2 wires fabricated by the mixing processes of IMD and PIT is close to that of the PIT-processed MgB2 wire (P0), 25.3%. These results suggest that the new method combining IMD and PIT can increase MgB2 layer thickness and hence yield higher MgB2 area fraction compared to IMD MgB2 wires.

Fig. 2-10 OM images on the transverse cross sections of (a) IMD-processed wire (M0), (b) PIT-processed wire (P0), and (c) the wire fabricated with new method combining IMD and PIT (M2)(Specification of the samples M0 to P0 are listed in table 2-2)
**Fig. 2-11(a)** and **Fig. 2-11(b)** show SEM images of the transverse and longitudinal cross sections of M2, respectively. A uniform MgB₂ layer was observed along the Fe sheath and a hole was found in the center of the wire. This result suggests that the mixing process of IMD and PIT can be applied to fabricate large-scale wires for practical applications. Some voids can be found in both transverse and longitudinal cross sections, which are produced by the volume shrinkage caused by the reaction between B powder and Mg powder as in the case of the PIT process. The voids have an ellipsoidal shape only in the longitudinal cross section, which is due to the elongation of Mg powder during the wire fabrication (groove-rolling and drawing) process.

**Fig. 2-11** SEM images of the (a) transverse and (b) longitudinal cross sections of the M2 MgB₂ wires (Specification of the samples M0 to P0 are listed in table 2-2)

**Fig. 2-12** shows SEM images of the longitudinal cross sections of MgB₂ wires of (a) M0, (b) M1, (c) M2, (d) M3, and (e) P0. The amount and size of the un-reacted B particles (dark areas) decreased and the voids in the MgB₂ layer were increased with increasing Mg powder addition, from **Fig. 2-12(a)** to (e). In **Fig. 2-12(b)**, the observed small amount of voids looks like bright lines, due to the small amount of Mg powder addition. In **Fig. 2-12(c)** and (d), a large amount of voids with ellipsoidal shape in the longitudinal direction can be observed. M3 (**Fig. 2-12(d)**) shows granular MgB₂ similar to P0 (**Fig. 2-12(e)**)). This is due to the large amount (25 mol%) of Mg powder addition to the B layer, which is a half of the amount of Mg powder of P0 (50 mol%). The added Mg powders in the B layer first react with B powders during the temperature-increase process and MgB₂ is formed resulting in shrinkage (voids). This first reaction produces voids near the formed Mg-B compound in the B layer, which is useful for the following Mg diffusion, thus improving the reaction between Mg and B. This is considered to be another mechanism of decreasing un-reacted B by Mg addition. Furthermore, B-rich regions existing far from the Mg rod, which can usually be found in IMD-processed MgB₂ wires [4, 5] even when the nano-sized B powders are used [10, 11], could also be decreased by this mixing process of IMD and PIT. Thus, we obtained a large thickness (almost 140 μm) MgB₂ layer without B-rich particles in this study.
Fig. 2-12 SEM images of the longitudinal cross sections of the MgB$_2$ wires, (a) M0, (b) M1, (c) M2, (d) M3, and (e) P0. All images were obtained after heat treatment (Specification of the samples M0 to P0 are listed in table 2-2)

Fig. 2-13(a) and (b) show $J_c$-B and $J_e$-B curves at 4.2 K for MgB$_2$ wires of (a) M0, (b) M1, (c) M2, (d) M3, and (e) P0, respectively. We found that the maximum $J_c$ ($4.9 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T, with M1) and $J_e$ ($5.8 \times 10^3$ A/cm$^2$ at 4.2 K and 10 T, with M2) values are both obtained by the new method combining IMD and PIT. All the $J_c$-B curves show almost the same slopes due to the similar carbon substitution for boron by the same 10 mol% SiC addition. The change in $J_c$ values is consistent with the change in microstructure observed by SEM, as shown in Fig. 2-12. With increasing Mg powder addition, the decrease of un-reacted B particles enhances $J_c$, while the...
increase of voids decreases $J_c$. The PIT-processed MgB$_2$ wire (P0) shows the lowest $J_c$ ($7.5 \times 10^3$ A/cm$^2$ at 4.2 K and 10 T) due to the largest amount of voids present in it.

Fig. 2-13 (a) $J_c$-$B$ and (b) $J_e$-$B$ curves at 4.2 K for the MgB$_2$ wires fabricated in this study (Specification of the samples M0 to P0 are listed in table 2-2)
The $J_c$ and $J_e$ values at 10 T and 4.2 K are compared in Fig. 2-14. As mentioned above, $J_c$ first increases and then decreases with increasing Mg powder concentration. $J_e$ also shows a similar trend but the maximum $J_e$ is obtained at a higher Mg concentration than the maximum $J_c$. With increasing Mg powder addition, the MgB$_2$ area fraction increased due to the increase in B layer thickness and the decrease in Mg rod diameter, leading to a higher $J_e$ value. Furthermore, the enhancement of $J_e$ by the Mg powder addition is much larger than that of $J_c$, which can also be explained by the increase in MgB$_2$ area fraction. Because $J_e$ values are a much more important parameter than $J_c$ values for practical applications, this new method is advantageous from the viewpoint of practical applications. We have not yet optimized parameters of this new method such as the amount of Mg powder addition, Mg rod size, sheath material and amount of B powder. Thus, the maximum $J_c$ and $J_e$ values can be further enhanced by optimizing these parameters.

Fig. 2-14 $J_c$ and $J_e$ values at 4.2 K and 10 T as a function of added Mg concentration, i.e. IMD, M1-M3, PIT (Specification of the samples M0 to P0 are listed in table 2-2)
2.4 Conclusions

In order to decrease the amount of un-reacted B particles in the IMD-processed MgB\(_2\) wires, we added Mg powder to the B powder layer to reduce the Mg diffusion distance. \(J_c\) increased for Mg concentration below 6 mol\% and decreased above 6 mol\% Mg addition for both undoped and 10 mol\% SiC-added IMD-processed MgB\(_2\) wires. The enhancement of \(J_c\) is due to the decrease of un-reacted B particles while the decrease of \(J_c\) above 6 mol\% Mg addition is due to the increase of porosity caused by the volume shrinkage resulting from the reaction between the Mg and B powders as in the case of PIT process.

A new hybrid method of IMD and PIT processes for fabrication of MgB\(_2\) wires was developed. This new method is that: Mg powder is added to the B layer of the IMD-processed MgB\(_2\) wires and the Mg rod diameter is decreased simultaneously to balance the ratio of Mg to B. \(J_c\) and \(J_e\) of this method are governed by factors including: the amount of un-reacted B, voids in the MgB\(_2\) layer, and MgB\(_2\) area fraction. In this study, the maximum \(J_c\) of 4.9 x 10\(^4\) A/cm\(^2\) at 10 T and 4.2 K was obtained for M1 (6 mol\% Mg addition), while the maximum \(J_e\) of 5.8 x 10\(^3\) A/cm\(^2\) was obtained for M2 (17 mol\% Mg addition). The enhancement of \(J_e\) by this process is much larger than that of \(J_c\). This is because both the addition of Mg powder and decrease in Mg rod diameter enable the increase in MgB\(_2\) layer thickness and, hence, the MgB\(_2\) area fraction is increased. The \(J_c\) and \(J_e\) values obtained in this study are not as high as in our previously reported data because I used low quality B powder in the present experiments. The use of high quality B powder is expected to increase \(J_c\) and \(J_e\) of the MgB\(_2\) wires fabricated by this new method. Furthermore, this process is expected to improve other properties (such mechanical properties, electrical magnetic properties) of IMD- and PIT-processed MgB\(_2\) wires.

Above all, the new method of combination of IMD and PIT developed in this chapter is expected to fabricate high performance MgB\(_2\) wires for practical applications.

In addition, enhancement of \(J_e\) is the technical problem, which will mainly be studied in the fabrication of products. Enhancement of physic properties, \(J_c\) are the main work for my Ph.D thesis. Thus the following chapter will not introduce new method developed in this chapter due to the new method increase \(J_c\) which is dependent of B powder we used.
References

Chapter 3 Fabrication of 37-filamentary IMD-processed MgB$_2$ wires

3.1 Introduction

As we know, the superconducting wires used for practical applications must be multi-filamentary wires for stability. The 37-filamentary MgB$_2$ wires for PIT process had been fabricated [1, 2]. But for IMD-process, 19 is the maximum filament number reported so far [3-6]. The fabrication of multi-filamentary IMD wire seems difficult because the Mg rod is not easily to cold-worked. This chapter describes the fabrication of 37-filamentary IMD-processed MgB$_2$ wires [7]. The critical current properties and microstructures of these wires were investigated.

3.2 Experimental details

An Mg rod (diameter: 2 mm) was placed into the center of a Ta tube (inner diameter: 3.5 mm, outer diameter: 6 mm). The oxide at the surface of the Mg rod was removed by an abrasive paper. The B powder (325-mesh, 99%) was packed into the space between the Ta tube and the Mg rod for the undoped wires, and a mixture of B powder and 10 mol% nano-sized SiC powder was used for the SiC-added wires. The composite was then cold worked (groove rolling and drawing) into a wire with diameter of 1.6 mm. The wire was then cut into 37 pieces of short wires, which were bundled and inserted into a Cu-20%Ni tube (inner diameter: 11.2 mm, outer diameter: 20 mm) to form a new composite. The new composite was then cold worked as above into a 37-filamentary wire (Ta-37) with diameters of 1.6 mm and 1.3 mm (more than 1 meter length for both wires) as shown in Fig. 3-1. The wires were then cut into short wires with a length of 4 cm for the heat treatment. Three kinds of heat treatment processes (shown in Fig. 3-2) were used in this work, denoted #1, #2, and #3. The process #1 consists of the temperature rising from room temperature to 640 °C in 1 hour, holding the temperature at 640°C for 5 hours, and then cooling to room temperature in the furnace. The process #2 consists of a temperature increase to 670 °C in 1 hour and holding at 670 °C for 3 hours, and then cooling to room temperature in the furnace. The process #3 consists of a temperature increase to 640 °C in 1 hour, a further increase to 670 °C in 3 hours, holding at 670 °C for 2 hours, and then cooling to room temperature. The short wires were wrapped with Zr foil and heat treated under Ar gas atmosphere (about 1 atm).
The mono- and 7-filamentary IMD-processed MgB$_2$ wires with a Ta-inner sheath and a Cu-Ni outer sheath were also fabricated for comparison. And they were termed as Ta-mono and Ta-7, respectively. Both the Ta-7 and Ta-mono are SiC-added wires, and with a diameter of 1.3 mm. The wire fabrication details of Ta-mono and Ta-7 have already been reported in our previous papers [4-6].

Fig. 3-1 Fabrication process of 37-filamentary IMD-processed MgB$_2$ wires

Fig. 3-2 Heat treatment processes for IMD-processed 37-filament MgB$_2$ wires
3.3 Results and discussion

Fig. 3-3 (a) shows SEM images of the transverse cross section of the IMD-processed 37-filamentary wire (center) and 4 filaments of the wire (surrounding). MgB$_2$ is formed along the inner wall of the Ta sheath in each filament. A hole is formed at the center of each filament due to Mg diffusion into the B layer. The hole is filled with resin during the polishing process. The filament sizes are small, and with a diameter of less than 100 μm. The MgB$_2$ area fraction is less than 2% in this experiment, which is smaller than that in the mono- and 7-filament IMD-processed MgB$_2$ wires in our previous work [8-11]. The low MgB$_2$ area fraction for the IMD-processed multi-filament MgB$_2$ wires is mainly due to (1) the thick Ta and Cu-Ni tubes, and (2) the hole generated in the center of each filament. Increase of the MgB$_2$ fraction of IMD-processed multi-filament MgB$_2$ wires is now under investigation. Fig. 3-3 (b) shows the EDS element mapping images of one filament of Fig. 3-3(a). The Mg completely diffused to B layer to form MgB$_2$. There is no concentration difference for Mg in the whole MgB$_2$ layer. This is because the diffusion distance of Mg in the filament less than 10 μm caused a full reaction between Mg and B. The MgO region can be found in inner wall of MgB$_2$ hole. This MgO region suggests that the Mg is left even after full reaction with B, which indicates that the MgB$_2$ area fraction could be further increased by optimizing the Mg rod diameter and B layer thickness. The carbon in the mapping is considered to be caused by the resin introduced during the polishing process.
Fig. 3-3 (a) SEM images of IMD-processed 37-filament MgB$_2$ wires and its filaments, and (b) the elements mapping for one filament of (a)
Fig. 3-4(a) shows the $J_e$ value at 4.2 K and 10 T of the IMD-processed 37-filament MgB$_2$ wires with the different heat treatment conditions shown in Fig. 3-2. The SiC-added wires show higher $J_e$.
values than those of the undoped wires. This is because carbon substitution causes impurity scattering, thereby, enhanced the upper critical field \((B_{c2})\), and hence enhancement of critical current properties in high fields such as 10 T. The 1.6 mm diameter wires show higher \(J_c\) values than that of the 1.3 mm diameter wires for both undoped and SiC-added wires. This is considered that some filaments of the 1.3 mm diameter wires are so small that MgB\(_2\) is no longer uniformly formed along the inner wall of the Ta sheath, while uniform MgB\(_2\) along the inner wall of the Ta sheath is formed for the 1.6 mm diameter wires in this research. Uniform MgB\(_2\) with 1.3 mm diameter could be obtained by optimizing parameters such as the Mg rod diameter, B layer thickness, and thickness of the sheaths. The optimized heat treatment conditions for undoped and SiC-added wires are different. The \(J_c\) values for the SiC-added wires are sensitive to the heat treatment conditions, and the #3 conditions can yield the highest \(J_c\). For the undoped wires, #1 yielded the highest \(J_c\) values, however, the differences among the three conditions are small.

The \(J_c\)-\(B\) curves at 4.2 K for the 1.6 mm diameter undoped and SiC-added wires are shown in Fig. 3-4(b). All of the SiC-added wires and undoped wires have similar slopes, respectively. This suggests that the amount of carbon substitution in boron sites is independent of the heat treatment conditions used in this experiment. The highest \(J_c\) in all measured magnetic fields for the SiC-added wires was obtained by the #3 heat treatment condition, and the #1 for the undoped wires. The nano-sized SiC particles affect the reaction between Mg and B and are responsible for the \(J_c\) difference of SiC-added wires, though the details remain unclear.

Fig. 3-5 shows \(J_c\)-\(B\) curves at 4.2 K for the IMD-processed MgB\(_2\) wires with the same 10 mol\% SiC addition but with different filament numbers, and under the same heat treatment condition (#3). The details of compared wires are listed in table 3-1. The \(J_c\)-\(B\) curves for all samples show the same slopes due to the same amount of carbon substitution for boron in all of the samples. The 37-filamentary IMD-processed MgB\(_2\) wires show the highest \(J_c\) at all measured magnetic fields, achieving a value of \(7.6 \times 10^4\) A/cm\(^2\) \((I_c = 27\) A\) at 4.2 K and 10 T. The Ta-7 wire shows a slightly lower \(J_c\) (about \(7.1 \times 10^4\) A/cm\(^2\) at 4.2 K and 10 T) than the Ta-37 wires but higher than that for the Ta-mono wires (\(6.6 \times 10^4\) A/cm\(^2\) at 4.2 K and 10 T).
Fig. 3-5 $J_c$-$B$ curves of the IMD-processed MgB$_2$ wires with different filaments at 4.2 K

(Specification of the samples are listed in table 3-1)

Table 3-1. The details of compared wires in Fig. 4

<table>
<thead>
<tr>
<th></th>
<th>Ta-mono</th>
<th>Ta-7</th>
<th>Ta-37</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (mm)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>B layer thickness (µm)</td>
<td>&lt; 100</td>
<td>&lt; 50</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>MgB$_2$ area fraction (%)</td>
<td>5%</td>
<td>3%</td>
<td>1.8%</td>
</tr>
<tr>
<td>$J_c$ at 4.2 K and 10 T (A/cm$^2$)</td>
<td>66,000</td>
<td>71,000</td>
<td>76,000</td>
</tr>
</tbody>
</table>

In order to investigate the difference in $J_c$ between the Ta-37 and Ta-mono wires in Fig. 3-5, their transverse cross sectional microstructures were observed with SEM. Fig. 3-6(a) and 6(b) show SEM images of MgB$_2$ layers near the Ta sheath and near the hole of the IMD-processed Ta-mono MgB$_2$ wires, respectively. There are a number of dark spots with sizes of 1-10 µm in the MgB$_2$ layers. I used the SEM-EDX to observe the different spots in Fig. 3-6 (b), the characteristic spectrum details of B (B k), C (C k), Mg (Mg k) and Si (Si k) are listed in table 3-2. The atomic ratio of B decreases and Mg increases from spot 1 (the deep dark spot), to spot 2 (dark spot), and then to spot 3 (normal region, also MgB$_2$ layer). By comparing the ratio (at%) Mg:B among the three spots, and with spot
3 identified as normal MgB$_2$ layer, we see that spot 3 is the most Mg-rich, much higher than the stoichiometric ratio of 1:2. I think this is because it is difficult for EDX to detect the light elements such as C and B, so the B and C are underestimated. This suggests that Mg is overestimated because the atomic ratio adds up to 100% for each spot. However, the ratio of Mg to B is expected to be a good indicator to estimate that the dark spots are un-reacted B particles or B-rich region, which is consistent to our previous research [9, 11]. Fig. 3-6(c) and 3-6(d) show SEM images of two filaments of the Ta-37 wires. There are also unreacted B particles in the MgB$_2$ layer, however, the average size of these is much smaller than that of the Ta-mono wires. The thickness of the MgB$_2$ layer for the Ta-mono wire is around 100 µm, while that of Ta-37 is mostly less than 20 µm. The smaller thickness of the MgB$_2$ layer in Ta-37 indicates a shorter Mg diffusion distance, which leads to smaller-sized unreacted B particles. These smaller-sized unreacted B particles in Ta-37 are mainly responsible for its higher $J_c$, shown in Fig. 3-5.

![SEM images](image1.png)

Fig. 3-6 SEM images in transverse cross-section of Ta-mono (a) near the Ta sheath and (b) near the hole (spectrum are observed for spots 1, 2 and 3), (c) Ta-37 filament 1, and (d) Ta-37 filament 2.
Table 3-2. The characteristic element spectrum details of B (B k), C (C k), Mg (Mg k) and Si (Si k) for Fig. 5(b)

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>spot 1</th>
<th>spot 2</th>
<th>spot 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>B k</td>
<td>50.92</td>
<td>37.95</td>
<td>9.88</td>
</tr>
<tr>
<td>C k</td>
<td>6.43</td>
<td>5.78</td>
<td>9.91</td>
</tr>
<tr>
<td>Mg k</td>
<td>42.04</td>
<td>54.06</td>
<td>70.94</td>
</tr>
<tr>
<td>Si k</td>
<td>0.61</td>
<td>2.21</td>
<td>9.27</td>
</tr>
</tbody>
</table>

Fig. 3-7(a) shows the temperature dependence of the $J_c$-$B$ curves for SiC-added 37-filament wires fabricated with the IMD process. At 20 K, the $J_c$ value is about $1.1 \times 10^5$, $0.6 \times 10^5$, and $0.3 \times 10^5$ A/cm² at 3 T, 4 T, and 5 T, respectively. The $J_c$ value is about $2 \times 10^5$ A/cm² at 20 K and 3 T. $J_c$ values higher than $1.0 \times 10^5$ A/cm² are observed at 4.2 K at 9 T, 10 K at 7 T, 15 K at 5 T, and 20 K at 3 T. The temperature dependence of $J_c$ for undoped (heat treatment condition: #1) and 10 mol% SiC-added (heat treatment condition: #1) 37-filament MgB₂ wires is compared in Fig. 3-7(b). The SiC-added wire shows higher $J_c$ at both 4.2 K and 15 K in all measured magnetic fields, while the undoped wire shows higher $J_c$ at 30 K in all measured magnetic fields. At 20 K, the SiC-added wire shows higher $J_c$ in fields higher than 4 T, while it shows lower $J_c$ in fields lower than 4 T. $J_c$ at 20 K and 3T for the undoped wires is about $1.6 \times 10^5$ A/cm², while $J_c$ is about $2.8 \times 10^5$ A/cm². These results reveal that SiC-addition has two effects: One is carbon substitution for boron, which enhances $B_{c2}$ and increases $J_c$ in high magnetic fields. The other is the decrease in $T_c$, which decreases $J_c$ at high temperatures and low magnetic fields. This suggests that the use of undoped or SiC-added wires for practical applications depends on the application temperature and magnetic field. Fig. 3-7 (c) shows the dependence of $I_c$ on the temperature (higher than 30 K) at the self-field for both undoped and SiC-added IMD-processed 37-filament MgB₂ wires. The undoped wires show higher $I_c$ than the SiC-added wires at all temperatures higher than 30 K. At 30 K, the $I_c$ is about 155 A ($J_c$: $4.4 \times 10^5$ A/cm²) for the undoped wires and 26 A ($J_c$: $7.3 \times 10^4$ A/cm²) for the SiC-added wires. The difference in $I_c$ at temperatures higher than 30 K is mainly due to the difference in $T_c$, 38.2 K for the undoped wires and about 33.3 K for the SiC-added wires.
(a) IMD Ta-37 SiC-added MgB\textsubscript{2} wires

(b) Dot line: undoped
Solid line: 10 mol\% SiC-added
Fig. 3-7 Temperature dependence of the $J_c$-$B$ curve for (a) SiC-added, (b) both undoped and SiC-added IMD-processed 37-filament MgB$_2$ wires, and (c) temperature dependence of $I_c$ on the temperature (higher than 30 K) at the self-field for both undoped and SiC-added IMD-processed 37-filament MgB$_2$ wires.

### 3.4 Conclusions

We successfully fabricated 37-filament MgB$_2$ wires with IMD process in this study. The fabrication conditions, impurity addition, critical current properties, and microstructural characteristics are investigated. Compared to mono-filamentary and 7-filamentary wires, higher critical current density was obtained for the 37-filamentary wire, which is considered to be due to the decrease of Mg diffusion distance by the increase of the filament numbers. The filaments size of as small as ~100 μm was obtained, although the Mg rod is considered to be difficult to be cold-worked. This study suggests that the IMD process can be used to fabricate large-scale MgB$_2$ wires for practical applications. Optimization of the starting composite materials (such as the Mg rod diameter, thickness of the B layer, thickness of the Ta tube, and thickness of the Cu-Ni tube) is expected to increase the MgB$_2$ superconducting area, which will be investigated in future work.
References

Chapter 4 Enhancement of critical current properties of IMD-processed MgB$_2$ wires by SiC and liquid aromatic hydrocarbon co-addition

4.1 Introduction

As introduced in Chapter 1, C-containing impurity addition (especially SiC addition), originally developed for the PIT process [1-4], is also effective in enhancing in-field $J_c$ values of IMD-processed MgB$_2$ wires. Hur et al. fabricated IMD-processed MgB$_2$ wires with SiC addition and obtained a $J_c$ of 41,000 A/cm$^2$ at 4.2 K and 10 T [5]. Our group [6-8] fabricated multi-filamentary IMD wires with SiC addition, and the $J_c$ of MgB$_2$ layer reached as high as 9.9×10$^4$ A/cm$^2$ at 4.2 K and 10 T [7, 8].

For PIT process, Yamada et al. reported that the co-addition of ethyltoluene and SiC give further improvement of in-field $J_c$ [9, 10] of MgB$_2$ wires, and they obtained a very high $J_c$ of 4.5×10$^4$ A/cm$^2$ at 4.2 K and 10 T by the co-addition of ethyltoluene and SiC, and applying hot pressing [10].

In this study, I tried the SiC and p-ethyltoluene co-addition to the IMD-processed MgB$_2$ wires. I also tried two other aromatic hydrocarbons, toluene and p-dimethylbenzene, which have the similar molecule structure as p-ethyltoluene. The details for this chapter are described on our previous paper [11, 12].

4.2 Experimental details

B (99%, 325-mesh) and 10 mol% nano-SiC (a few tens of nanometer size) powders were well ground in a mortar. Liquid aromatic hydrocarbon was then mixed with the starting powders (B+SiC) in the mortar, and then the mixture was kept in the draft chamber till air-dried. After air-drying, the mixture were re-ground into uniform powder. The mixed powder was packed into the gap between a Fe tube and a pure Mg rod which was coaxially inserted into the Fe tube. Then the composite was groove-rolled into a rod shape and drawn into a wire with diameter of 1.2 mm. The wire was cut into short pieces of 40 mm length, which were wrapped with Zr foils and heat treated under Ar gas atmosphere at temperatures of 640°C, 670°C and 700°C for 3 h. The details of
fabrication process were described in Chapter 1. We also fabricated wires without addition (pure), and with nano-SiC addition for comparison. Furthermore, the wire with toluene addition was also fabricated for comparison.

The microstructure of the samples was investigated by optical microscope and x-ray diffraction (XRD). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out with the Hitachi SU-70 and JEM-2100F, respectively. The samples for TEM observation is the 100 nm thin film of a longitudinal cross section of the wire produced by a focused ion beam (FIB).

The transport critical current ($I_c$) for the wires was measured at temperatures of 4.2, 10, 15, 20, 25, and 30 K in magnetic fields below 13 T using a four-probe resistance method. The value of $J_c$ for each wire was calculated by dividing $I_c$ by the whole MgB$_2$ area including B-rich region. The $J_e$ was calculated by dividing $I_c$ by the entire wire area in the transverse cross section.

### 4.3 Results and discussion

#### 4.3.1 Enhancement of $J_c$ and $J_e$ for MgB$_2$ wires by SiC and liquid aromatic hydrocarbon co-addition

Fig. 4-1(a), 1(b) and 1(c) show the $J_c$-B properties of the five samples (pure, SiC addition and three co-addition: SiC+toluene, SiC+ethyltoluene and SiC+dimethylbenzene) heat treated at 640 °C, 670 °C and 700°C for 3 h, respectively. The $J_e$ value of SiC added wires is superior to that of pure wires in the whole regions of magnetic field and further improvement is observed for SiC+toluene co-added wires. These are independent of heat treatment temperature. On the other hand, SiC added wires and SiC+toluene co-added wires show high $J_e$ values in the high-field region with comparable field dependence which is smaller than that of pure wires. These results are probably due to the C substitution for B which enhances $B_{c2}$, and hence the $J_c$ [13] (here $J_e$) in the wires with SiC addition and SiC+toluene co-addition.

At 640°C, SiC+toluene co-added wires show the best $J_e$ values which are about twice as high as that of SiC added wires in all fields. The SiC+ethyltoluene co-addition firstly reported for the PIT processed tape by Yamada et al [9, 10] brings about a 10% enhancement in $J_e$, compared with SiC added wires in all fields. SiC+dimethylbenzene co-added wires show lower $J_e$ value than SiC added wires in 10 and 12 T while higher in 8 T. It is interesting to note that the pure wires show higher $J_e$
value than the SiC+ethyltoluene co-added wire and SiC+dimethylbenzene co-added wire by about 14% and 33%, respectively, in 6 T while the opposite results are observed above 6 T.

At 670°C, the $J_c$ value of SiC+dimethylbenzene co-added wires is about 3,700 A/cm² at 4.2 K and 10 T. The $J_c$ value at 8 T may be under-estimated because the measured $I_c$ was deteriorated due to temperature rise of samples which is caused by the Joule heating at current contact. The sample was damaged and burned at the 8 T measurement, and therefore we couldn’t carry out the $I_c$ measurement at 6 T. The SiC+toluene co-addition also brings about $J_c$ enhancement by about 20%, compared with SiC addition in all magnetic fields. SiC+ethyltoluene co-added wire shows $J_c$ value lower than SiC added wire by 50% in all fields.

At 700°C, the result is similar to that at 670°C. The SiC+dimethylbenzene co-added wire shows the best $J_c$ property in all fields although the $J_c$ value in 6 T may be also under-estimated due to the Joule heat generation. The SiC+toluene co-added wire shows higher $J_c$ value than SiC added wire by about 20%, and SiC added wire also shows higher $J_c$ value than SiC+ethyltoluene added wire by about 20% in all fields. Comparing to pure wires, the SiC+dimethylbenzene co-added wire shows about twice $J_c$ value in 6 T while 20 times in 12 T.

The best $J_c$ values calculated for the cross-sectional area of MgB$_2$ layers of each wire are compared in Fig. 4-1(d). SiC+toluene co-added wire heat treated at 640°C shows the best $J_c$ property in all fields, and the $J_c$ value at 4.2 K and 10 T is about 4.8 x 10⁴ A/cm², which is higher than those of SiC added IMD processed wires reported by Hur et al [5] and other PIT-processed wires and tapes reported so far. Furthermore, the B powder I used has lower quality (99.8%, 325-mesh) than those used by others [5-8]. The small field dependence observed for wires with additive suggests that C substitution for B in MgB$_2$ occurred and enhanced critical current properties in high fields. The $J_c$ of the SiC+ethyltoluene co-addition is the lowest among wires with the additives, which is different from the results obtained by Yamada et al in the PIT-processed MgB$_2$ tapes. This difference is considered to be due to the difference of reaction process between the IMD- and PIT-processed MgB$_2$ wires.
(a) Magnetic field (T)

(b) Magnetic field (T)
Fig. 4-1  $J_c$-$B$ curves (at 4.2 K) of various IMD-processed MgB$_2$ wires heat treated at (a) 640°C, (b) 670°C and (c) 700°C for 3 hours, and (d) $J_c$-$B$ curves (at 4.2 K) of various IMD processed MgB$_2$ wires: optimized heat treatment temperature was chosen for each wire.
As introduced above, SiC + dimethylbenzene co-added samples showed the effective enhancement of $J_c$ of the IMD-processed MgB$_2$ wires. I measured the $J_c$ and $J_e$ properties of the SiC+ dimethylbenzene co-added wires at temperatures of 4.2, 10, 15, 20, 25, and 30 K in the magnetic fields below 13 T using a four-probe resistance method. The $J_c$ of pure wires are also measured. Fig. 4-2 (a) and (b) show the $J_c$-$B$ curves and $J_e$-$B$ curves of SiC+dimethylbenzene co-added IMD-processed MgB$_2$ wires, respectively. The $J_c$ at 4.2 K and 10 T for the sample is $4.5 \times 10^4$ A/cm$^2$. At 20 K, its $J_c$ is about $5.3 \times 10^3$ at 5 T and $1.0 \times 10^5$ A/cm$^2$ at 4 T. At 30 K and 0 T, its $J_c$ is about the $1.2 \times 10^5$ A/cm$^2$. At 20 K and 5 T its $J_c$ is $4.2 \times 10^4$ A/cm$^2$. The $J_c$-$B$ curves for the pure wires are shown in the Fig. 4-2 (c) for comparison. Its $J_c$ values are lower than that of SiC+ dimethylbenzene wires at high measured field and low temperature, while higher at low field and high temperature. At 30 K and 0 T, its $J_c$ is about $1.3 \times 10^5$ A/cm$^2$. 

(a)
Fig. 4-2 (a) the $J_c$-$B$ curves and (b) the $J_e$-$B$ curves of SiC+dimethylbenzene co-added IMD-processed MgB$_2$ wires, respectively. (c) the $J_c$-$B$ curves of pure IMD-processed MgB$_2$ wires.
4.3.2 Study on the mechanism of the $J_c$ enhancement of MgB$_2$ wires by SiC and toluene co-addition

In order to study the mechanism of $J_c$ increase properties by these additives, I compared the $J_c$ and microstructure of pure, toluene-added, SiC-added, and SiC and toluene co-added IMD-processed MgB$_2$ wires. The wires in the following experiment were heat treated at 670 °C for 3 hours. This temperature condition caused full reaction between Mg and B, hence, it is better to obtain critical current properties with good reproducibility.

Fig. 4-3 show the $J_c$-B curves of pure wire and wires with toluene addition, SiC addition and SiC+toluene co-addition. The $J_c$ of the added-wires were superior to that of pure wires. We could not measure $I_c$ under 8 T of SiC+toluene co-added wires and SiC-added wires because the current was so high (both wires had an $I_c$ value of more than 200 A at 6 T) that the wire might have burned out due to the Joule heat at the current contact. The SiC+toluene co-added wire showed the highest $J_c$ value above 8 T and the smallest field dependence in all wires. The $J_c$ value of SiC+toluene co-added wires was about $5 \times 10^4$ A/cm$^2$ at 10 T and 4.2 K, which is 1.2 times higher than that of SiC-added wires, but, at 8 T and 4.2 K, the value was almost the same. SiC-added wires showed a notable higher $J_c$ value and smaller magnetic field dependence than toluene-added wires. The $J_c$ value of toluene-added wire was about 17% of that of SiC-added wires but 1.4 times of that of pure wires at 10 T and 4.2 K. The magnetic field dependence of toluene-added wires was larger than that of SiC-added wires and smaller than that of pure wires.

![Fig. 4-3 $J_c$-B curves of IMD-processed MgB$_2$ wires with different additives](image-url)
Fig. 4-4 shows the XRD pattern of all wires fabricated in this experiment. Strong Fe peaks are from the Fe sheath. The peaks of Mg$_2$Si which is formed by the reaction between SiC and Mg are also clearly observed in the SiC-containing additives (SiC addition and SiC+toluene co-addition). MgO may be formed by the reaction during the heat treatment. The 110 peaks of MgB$_2$ are shifted toward high-angle sides by additives (toluene, SiC, and SiC+toluene). The a-axis, c-axis lattice parameter, and amount of carbon substitution for boron (x in the Mg(B$_{1-x}$C$_x$)$_2$) calculated using the results of Lee et al. [14] are listed in Table 4-1. The values of the c-axis almost remain the same, while the a-axis decreased with the additives. The amount of carbon substitution for boron in the toluene addition was about 0.01, and that of SiC addition was 0.037, while, in the SiC+toluene co-addition, it was 0.042, which is smaller than the sum of the SiC addition and toluene addition (0.047). This may be due to the reason that SiC and toluene competed and suppressed each other in the reaction process of carbon substitution for boron. This carbon substitute for boron seems to be one of the main reasons for the $J_c$ enhancement [13] in applied magnetic fields of our IMD-processed MgB$_2$ wires.

![Fig. 4-4 XRD patterns of IMD-processed MgB$_2$ wires with different additives](image)

**Table 4-1.** The a-axis, c-axis, and amount of carbon substitution for boron of IMD-processed mono-core MgB$_2$ wires with different additives

<table>
<thead>
<tr>
<th>Additives</th>
<th>a-axis (Å)</th>
<th>x of Mg(B$_{1-x}$C$_x$)$_2$</th>
<th>c-axis (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>3.08583</td>
<td>0</td>
<td>3.52058</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.08142</td>
<td>0.01</td>
<td>3.52564</td>
</tr>
<tr>
<td>SiC</td>
<td>3.06958</td>
<td>0.037</td>
<td>3.52317</td>
</tr>
<tr>
<td>SiC+toluene</td>
<td>3.06726</td>
<td>0.042</td>
<td>3.52129</td>
</tr>
</tbody>
</table>
Fig. 4-5(a), (b), (c), and (d) show the SEM images on the transverse cross section of all wires. The grain size of doped wires (Fig. 4-5(b), (c), and (d)) seems smaller than that of pure wires (Fig. 4-5(a)); in particular, the grain size of wires with the toluene-containing addition (Fig. 4-5(b) and (d)) is much smaller. A small grain size can increase the grain boundary area, which increases the flux pinning force, and hence leads to $J_c$ enhancement. This may be another reason why toluene addition increases $J_c$ values.

Fig. 4-5 SEM images of IMD-processed MgB$_2$ wires (a) with no addition, (b) with toluene-addition, (c) with SiC-addition, (d) with both SiC and toluene co-addition.
4.3.3 The microstructure analysis and a proposal of new mechanism of enhanced $J_c$ of MgB$_2$ wire by SiC addition

As introduced above, SiC addition is mainly responsible for the $J_c$ enhancements of IMD-processed MgB$_2$ wires. In this section, the microstructures of SiC-added IMD-processed MgB$_2$ wires by SEM and TEM are shown. The undoped wires are also presented for comparison.

**Fig. 4-6** show the representative SEM image (Fig. 4-6 (a)) and its EDX element mapping images of SiC-added IMD-processed MgB$_2$ layer. **Fig. 4-6 (b-f)** show B, O, Mg, Si, and C elements, respectively. The EDX images indicated that the dark spots are the un-reacted B particles. These un-reacted B particles are not superconductive, so the decrease of this un-reacted B powder can increase the critical current properties of IMD-processed MgB$_2$ wires.

![Representative SEM image(a), EDX element mapping images of B, O, Mg, Si and C elements (b - f), on the longitudinal cross sections of SiC-added IMD-processed MgB$_2$ wires](image-url)
Fig. 4-7(a) is a TEM bright field image of the MgB$_2$ layers of SiC-added IMD-processed MgB$_2$ wires. The grain size is mostly less than 100 nm, which is consistent with the SEM images in Fig. 4-5. Fig. 4-7(b) shows typical high-resolution image of region A in Fig. 4-7(a), and its diffraction pattern is shown in the Fig. 4-7(c). We can see that MgB$_2$ and Mg$_2$Si crystals exist in the region A. Fig. 4-7(d) shows the high-resolution image of region B in Fig. 4-7(a). Its diffraction pattern (Fig. 4-7(e)) show that this region is in amorphous state. For the SiC-added IMD-processed MgB$_2$ wires, the unreacted B particle is mostly the amorphous state, which is consistent with the SEM-EDX images of Fig. 4-6.

![TEM image of IMD-processed mono-core MgB$_2$ wires with SiC addition](image)

**Fig. 4-7** (a) TEM image of IMD-processed mono-core MgB$_2$ wires with SiC addition, (b) high resolution image of region B in (a), (c) diffraction pattern of (b), (d) high resolution image of region C in (a), (e) diffraction pattern of (d)
Fig. 4-8 (a) and (b) show the TEM images, elemental maps by EDS and energy filtering image (EFI) of pure wires and SiC-added wires, respectively. The amorphous regions are proved to be the un-reacted B particles by EFI. This is consistent with the Fig. 4-6 and Fig. 4-7. The interesting point is that the oxide in the SiC-added wires seems to be more dispersed than that in the pure wires. Fig. 4-8 (c) and (d) show the schematic illustrations of the elemental distributions of pure wires and SiC-added wires, respectively. For pure wires, the MgO has a thin layer around MgB₂ grains, in which the un-reacted B particles can be also observed. While for the SiC-added wires, MgO with nano size is dispersed in the MgB₂ grains. The nano-sized MgO in SiC-added wires can work as flux pinning center to increase $J_c$, while the MgO thin layer in pure wires prevents the supercurrent. Dispersion of MgO in MgB₂ layer is one reason for the $J_c$ enhancement of IMD-processed MgB₂ wires by SiC addition.
Fig. 4-8 Elemental maps by EDS and EFI of (a) pure wires and (b) SiC-added wires; the schematic illustrations of the elemental distributions of (c) pure wires and (d) SiC-added wires.
4.4 Conclusions

The effect of the addition of both SiC and liquid aromatic hydrocarbon (toluene, p-ethyltoluene and p-dimethylbenzene) to the IMD-processed MgB$_2$ wires was investigated. The $J_c$ properties are enhanced by co-addition of SiC with toluene and dimethylbenzene, but not so good for ethyltoluene. The highest $J_e$ and $J_c$ at 4.2 K and 10 T obtained in this work are 3,700 A/cm$^2$ and 48,000 A/cm$^2$, respectively, which were achieved for the SiC+dimethylbenzene co-added wires heat treated at 670°C for 3 hours. The results indicate that the co-addition of SiC and liquid aromatic hydrocarbon is one of the promising methods to improve the $J_c$ as well as $J_e$ of the IMD processed MgB$_2$ wires.

I also studied the microstructure in order to investigate the mechanism of $J_c$ enhancement. I observed the microstructures of the wires with SiC and/or toluene additives by TEM and SEM. The SiC and toluene co-addition increased the carbon substitution for B in the MgB$_2$ and the toluene addition decreased the grain size. They are considered to be mainly responsible for the $J_c$ enhancement by the co-addition of SiC and toluene. Furthermore, I speculate that (a) the liquid hydrocarbon make the mixture of SiC and B powder uniform, (b) the absorbed liquid aromatic on the B surface prevent B absorbing oxide, and (c) the liquid aromatic hydrocarbon absorbed on the B surface also prevent the growth of MgB$_2$ grain. These are also considered to contribute to the $J_c$ and $J_e$ enhancements. I also discovered by TEM that SiC addition distributed oxides in MgB$_2$ layer. This discovery is useful to explain the $J_c$ enhancement caused by SiC addition.
References


Chapter 5 Enhancement of $J_c$ properties of MgB$_2$ wires by pretreating carbon-coated nano-sized B powder with Dimethylbenzene

5.1 Introduction

The quality of B powder is crucial to $J_c$ of IMD-processed MgB$_2$ wires. The B powder I used in chapters 2-4 is not so good for its big size (325-mesh) and poor reactivity with Mg. In June of 2012, Li et al. [1] fabricated the IMD-processed MgB$_2$ wires (diameter: 0.55 mm) by using a special plasma-synthesized 2% carbon-coated B powder (Special Materials Inc., SMI B powder, particle size < 50 nm). And they obtained a high $J_c$ of $1.07 \times 10^5$ A/cm$^2$ and a high engineering $J_c$ ($J_e$) of $1.67 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T for different samples.

I also tried this SMI B powder, however, I didn’t obtain good results as theirs. After investigating the B powder, I found that many BCl$_3$ (source material for this B powder) exists in the B powder. Because dimethylbenzene is a good solvent for BCl$_3$, and our experiments in chapter 4 showed dimethylbenzene enhanced the $J_c$ of IMD-processed MgB$_2$ wires, I pre-treated the SMI B with dimethylbenzene to remove BCl$_3$. I found the dimethylbenzene decreased the BCl$_3$ in B powder and then I obtained higher $J_c$ values [2, 3]. The current transport properties and microstructures were investigated in this chapter. The details are described in my previous paper [3].

5.2 Experimental details

The following process (shown in Fig. 5-1) was carried out to remove residual BCl$_3$ from the SMI B powder. The powder was first ultrasonically mixed with C$_8$H$_{10}$, then the liquid was removed from the mixture by filtering, finally the remaining material was dried in a vacuum furnace at 100 °C. This powder is referred to SMI+D powder in this thesis.
The SMI+D powder was used to fabricate wires using two kinds of metal sheathing tubes, made from Fe or Ta, with an outer diameter of 6 mm and an inner diameter of 4 mm. Details of the fabrication process have been previously reported [2-8]. Usually, the diameter of 2 mm Mg rod was used for the Fe-sheathed wire fabricated with SMI B powders, and full-reacted MgB2 layer (with low MgB2 area fraction) was formed without B-rich region. In this experiment, we also tried the 1.8 mm diameter Mg rod for Fe-sheathed wire in order to increase the thickness of MgB2 layer and to obtain high \( J_c \). The Mg rod with a diameter of either 2 mm or 1.8 mm was inserted along the center of the Fe tube, and B powder was packed into the intervening space in the air. The composite was groove-rolled and then drawn into a wire with a diameter of 0.6 mm. Wires formed using Mg rods with diameters of 2 mm and 1.8 mm are referred to as the Fe-SMI+D-1 and Fe-SMI+D-2 wires, respectively. For the Ta-sheathed wire, the composite was first groove-rolled and drawn into a wire with a diameter of 4 mm. This was then inserted into a Cu-Ni tube with an outer diameter of 6 mm and an inner diameter of 4 mm, which was groove-rolled and drawn into a wire with a diameter of 0.6 mm. This Ta-sheathed wire is referred to as the Ta-SMI+D wire. For comparison, an Fe-sheathed wire was also fabricated using the SMI powder, and this is referred to as the Fe-SMI wire. All the fabricated wires were heat treated at 675 °C for 8 h in an Ar gas flow, which is the same temperature used by Li et al. [1]. The temperature was ramped up to 675 °C over the course of 1 h, and after the heat treatment, the wires were cooled in the furnace.

The transport critical current (\( I_c \)) for the wires was measured at temperatures of 4.2, 10, 15, 20, 25, and 30 K in magnetic fields below 13 T using a four-probe resistance method. The value of \( J_c \) for each wire was calculated by dividing \( I_c \) by the whole MgB2 area including B-rich region. The \( J_c \) was calculated by dividing \( I_c \) by the entire wire area in the transverse cross section.

Scanning electron microscopy (SEM) was carried out using a Hitachi SU-7. Energy dispersive X-ray spectroscopy (EDX) of powders was observed and analyzed by Genesis spectrum system of EDAX Inc., which is connected to SU-7. X-ray diffraction (XRD) analysis was carried out with Miniflex II of Rigaku. The TEM specimen was prepared using focused ion beam milling (JEOL JEM-FIB9320) and had a thickness of 100 nm. TEM and scanning TEM (STEM) observations were carried out using a JEOL JEM-2100F. Electron energy loss spectroscopy (EELS) images were obtained using a FEI Tecnai G2 F30.
5.3 Results and Discussion

5.3.1 Starting B powder

In this experiment, 4 mol% carbon-coated SMI B powder with nanometer-sized particles was first used in the IMD process. However, it was found that the MgB₂ wires fabricated using this powder exhibited a low critical current (Iₐ). An analysis of the powder indicated that it contained chlorine (Cl), which is thought to originate from the BCl₃ raw material used to produce the B powder. The SMI powder is produced using the following reaction [9]:

\[
2 \text{BCl}_3 + 3 \text{H}_2 \xrightarrow{RF \text{ plasma}} 2 \text{B} + 6 \text{HCl}
\]

However, residual BCl₃ adsorbed on the powder particles can react with humidity when exposed to air, decreasing the quality of the power and resulting in a low critical current in the fabricated MgB₂ wires.

Fig. 5-2 show the XRD pattern of IMD-processed MgB₂ wires fabricated with SMI powder (left), and the images of IMD-processed MgB₂ wires before heat treatment fabricated with SMI and SMI+D powders (right). The BCl₃ absorbed the humidity in the air to form acid, which is considered to be the reason for the rust on the surface of Fe sheath.

Fig. 5-2 The XRD pattern of IMD-processed MgB₂ wires before heat treatment fabricated with SMI powder (left), and the images of IMD-processed MgB₂ wires fabricated with SMI and SMI+D powders (right)
An elemental analysis of both the SMI and SMI+D powders was carried out using energy dispersive X-ray spectroscopy (EDX). As shown in Fig. 5-3, although both powders exhibited a Cl peak, its intensity relative to that of the main B peak was lower for the SMI+D powder. According to the manufacturer, the typical Cl content in SMI powder is from 0.5 to 1 at% [10]. The results of the elemental analysis are listed in table 5-1 for three different SMI and SMI+D powders (P1, P2, and P3). In table 5-1, the Cl content is likely to be highly over-estimated because the light elements B, C, and O are difficult to detect using EDX. However, the ratio of Cl to B is expected to be a good indicator of the relative Cl content of the different powders. From table 5-1, it can be seen that this ratio is consistently lower for the SMI+D powder, indicating that as expected, the pre-treatment with C₈H₁₀ decreases the Cl content in the SMI powder.

![Fig. 5-3 EDX spectra of (a) SMI powder, and (b) SMI+D powder](image)

**Table 5-1. Compositions of SMI and SMI+D powders obtained from EDX analysis**

<table>
<thead>
<tr>
<th>Element (At%)</th>
<th>SMI-P1</th>
<th>SMI-P2</th>
<th>SMI-P3</th>
<th>SMI+D-P1</th>
<th>SMI+D-P2</th>
<th>SMI+D-P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>B K</td>
<td>72.48</td>
<td>74.19</td>
<td>71.01</td>
<td>74.05</td>
<td>75.46</td>
<td>75.66</td>
</tr>
<tr>
<td>C K</td>
<td>11.65</td>
<td>10.85</td>
<td>14.54</td>
<td>16.56</td>
<td>13.35</td>
<td>13.73</td>
</tr>
<tr>
<td>O K</td>
<td>4.94</td>
<td>4.91</td>
<td>4.09</td>
<td>3.61</td>
<td>4.71</td>
<td>4.74</td>
</tr>
<tr>
<td>Cl K</td>
<td>10.93</td>
<td>10.05</td>
<td>10.36</td>
<td>5.78</td>
<td>6.48</td>
<td>5.87</td>
</tr>
</tbody>
</table>
Scanning electron microscopy (SEM) was also carried out on the powder samples, and the results are shown in Fig. 5-4. It can be seen that the SMI+D powder (Fig. 5-4 (b)) is somewhat agglomerated, with the agglomerates being up to 15 μm in size. It was found that because of this agglomeration, the powder could be more easily packed into a metal tube than the SMI powder (Fig. 5-4 (a)).

![Fig. 5-4 SEM images of (a) SMI powder, and (b) SMI+D powder](image)

### 5.3.2 Fabrication of wires

In this study, four kinds of wires with a diameter of 0.6 mm were fabricated using the IMD process. For two of the wires, SMI+D powder was used, together with a Mg rod with a diameter of either 2 mm or 1.8 mm and Fe sheath; these will henceforth be referred to as the Fe-SMI+D-1 and Fe-SMI+D-2 wires, respectively. In addition, a Ta-sheeted wire was produced using SMI+D powder (Ta-SMI+D) and a Fe-sheeted wire using SMI powder (Fe-SMI). Details of the fabrication process have been previously reported [2-8].

Fig. 5-5 (a-d) show transverse and longitudinal cross-sectional SEM images of the Ta-SMI+D and Fe-SMI+D-1 wires. For both types of wires, the MgB$_2$ layer thickness is fairly uniform due to almost complete reaction between the B and Mg. A hole is seen to run along the center of the wires, which in the case of the Fe-sheeted wire, is filled with some unreacted Mg and the resin used to mount the wires for SEM observations. The MgB$_2$ area fraction and the sheath area fraction for the wires fabricated in the present study are shown in table 5-2. The MgB$_2$ area fraction is about 7%, except for Fe-SMI+D-2, where it is 11.8% due to the smaller Mg rod diameter. The sheath area fraction for the Fe-sheeted wires is about 75%, while for the Ta-sheeted wire, the sheath (including the Cu-Ni and Ta) area fraction is about 85%. Fig. 5-5 (e, f) show transverse and longitudinal cross-sectional optical microscope images of Fig. 5-5 (c-d). The MgB$_2$ layer are orange color similar to Fig. 2-10(a), indicating that no B-rich region can be observed in the sample.
Fig. 5-5 Cross-sectional SEM images of (a), (b) Ta-SMI+D wire, and (c), (d) Fe-SMI+D-1wire, (e-f) optical microscope images of (c-d)

Table 5-2. MgB$_2$ area fraction and sheath area fraction for high-performance MgB$_2$ wires

<table>
<thead>
<tr>
<th>IMD-processed MgB$_2$ wires</th>
<th>Other U. wire 1</th>
<th>Other U. wire 2</th>
<th>Ta mono</th>
<th>Fe mono</th>
<th>Fe mono-1</th>
<th>Fe mono-2</th>
<th>Fe mono</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting powder</td>
<td>SMI</td>
<td>SMI+Dinitrol/Inconel</td>
<td>SMI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat treatment condition</td>
<td>675 °C/0.5 h</td>
<td>675 °C/8 h</td>
<td>675 °C/8 h</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter (mm)</td>
<td>0.55</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sheath material</td>
<td>Inner: Hb, outer: monel</td>
<td>Inner: Ta, Outer: Cu-Ni</td>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgB$_2$ area fraction (%)</td>
<td>67</td>
<td>65</td>
<td>83</td>
<td>76</td>
<td>75</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>FeB$_2$ area fraction (%)</td>
<td>10.1</td>
<td>18.8</td>
<td>7.1</td>
<td>7.9</td>
<td>11.8</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>$J_c$ (A/cm$^2$) @ 4.2 K &amp; 10 T</td>
<td>$1.07 \times 10^6$</td>
<td>$0.93 \times 10^6$</td>
<td>$1.83 \times 10^6$</td>
<td>$1.15 \times 10^6$</td>
<td>$0.83 \times 10^6$</td>
<td>$0.88 \times 10^6$</td>
<td>$0.68 \times 10^6$</td>
</tr>
<tr>
<td>$J_c$ (A/cm$^2$) @ 4.2 K &amp; 10 T</td>
<td>$0.97 \times 10^4$</td>
<td>$1.67 \times 10^4$</td>
<td>$0.84 \times 10^4$</td>
<td>$0.81 \times 10^4$</td>
<td>$0.98 \times 10^4$</td>
<td>$0.48 \times 10^4$</td>
<td></td>
</tr>
</tbody>
</table>
X-ray diffraction (XRD) analysis was carried out for the Fe-SMI and Fe-SMI+D-1 wires as shown in Fig. 5-6. The a- and c-axis lattice parameters were determined from the MgB$_2$(110) and MgB$_2$(002) peaks in the XRD pattern, respectively. The amount of carbon substitution for boron, and the $T_c$ value were then calculated from the lattice parameters based on the method of Lee et al. [11] The $T_c$ value for these wires was also directly measured using a 4-probe method. The lattice parameters, amount of carbon substitution for boron, and calculated and measured $T_c$ for the Fe-sheathed wires using SMI and SMI+D powders are summarized in table 5-3. The amount of C substitution for B (x in Mg(B$_{1-x}$C$_x$)$_2$) is 0.033 and 0.030 for the Fe-SMI and Fe-SMI+D-1 wires, respectively. This suggests that the C$_8$H$_{10}$ has little influence on C substitution for B, and hence on $T_c$. The measured $T_c$ values are seen to be consistent with the calculated values.

![X-ray diffraction (XRD) patterns for the Fe-SMI and Fe-SMI+D-1 wires](image)

**Fig. 5-6 X-ray diffraction (XRD) patterns for the Fe-SMI and Fe-SMI+D-1 wires**

<table>
<thead>
<tr>
<th></th>
<th>a-axis (Å)</th>
<th>c-axis (Å)</th>
<th>X in Mg(B$_{1-x}$C$_x$)$_2$</th>
<th>Calculated $T_c$ (K)</th>
<th>Measured $T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-SMI</td>
<td>3.071917</td>
<td>3.516894</td>
<td>0.033</td>
<td>33.2</td>
<td>33</td>
</tr>
<tr>
<td>Fe-SMI+D-1</td>
<td>3.073768</td>
<td>3.520671</td>
<td>0.030</td>
<td>33.7</td>
<td>33.2</td>
</tr>
</tbody>
</table>

Table 5-3. Lattice parameters, amount of carbon substitution for boron, and calculated and measured $T_c$ for Fe-sheathed wires using fabricated SMI and SMI+D powders.
5.3.3 Critical current properties

Fig. 5-7(a) and (b) show the \( J_c - B \) and \( J_e - B \) curves, respectively, for the different wires. Data for the high-\( J_c \) wire (B1) and high-\( J_e \) wire (B3) obtained by Li et al. [1] are also included for comparison. For all the wires fabricated in the present study, the \( J_c - B \) curves have similar slopes, suggesting a similar amount of C substitution for B, which is consistent with the results shown in Table 5-3. The Ta-SMI+D and Fe-SMI+D-1 wires both show excellent \( J_c \) values. The \( J_c \) value for the Ta-SMI+D wire at 10 T and 4.2 K is about \( 1.2 \times 10^5 \) A/cm\(^2\), which is the highest \( J_c \) reported for MgB\(_2\) wires. However, all of the \( J_e \) values are lower than the highest value obtained by Li et al. [1] (about \( 1.67 \times 10^4 \) A/cm\(^2\)). For the wires fabricated in the present study, the highest \( J_e \) value is about \( 1 \times 10^4 \) A/cm\(^2\) for Fe-SMI+D-2. However, the \( J_e \) value for Fe-SMI+D-2 is lower than that for Fe-SMI+D-1, which is due to the presence of less Mg. Thus, some B-rich region remained and decreased \( J_c \). As shown in Table 5-2, the wires fabricated in the present study had a higher sheath area fraction and a smaller MgB\(_2\) area fraction than those fabricated by Li et al. [1]. Decreasing the sheath area fraction by the use of a thin metal tube and increasing the MgB\(_2\) area fraction by optimizing the starting B layer could therefore lead to an increase in \( J_e \). The wires fabricated using the SMI+D powder have higher \( J_c \) and \( J_e \) than those fabricated using the SMI powder. The SMI powder is so fine that it is not easy to insert it into the space between the Mg rod (diameter: 2 mm) and the sheath (inner diameter: 4 mm). This leads to a lower-density B layer and consequently a lower \( J_c \) and \( J_e \). Since the addition of C\(_8\)H\(_{10}\) causes agglomeration of the powder particles and makes the powder easier to be packed, the B layer density becomes higher. Another reason for the higher \( J_c \) for the SMI+D wires may be the reduced amount of Cl, although the mechanism is unclear at present.
Fig. 5-7 Comparison of (a) $J_c$-$B$, and (b) $J_e$-$B$ curves for IMD-processed MgB$_2$ wires at 4.2 K

(Specification of the samples are listed in table 5-2)
Fig. 5-8 shows the measured $J_c$ and $J_e$ values for the Fe-SMI+D-1 wire at different temperatures and magnetic fields. For comparison, the results for Ta-sheathed 7-core (Ta-7) wires previously fabricated with high-quality B powder and added SiC [7, 8] are shown by the dotted lines. In Fig. 5-8(a), the $J_c$-$B$ curve for the most commonly used Nb-Ti metallic superconducting wire [12] is also shown by a dotted line. The slope of the $J_c$-$B$ curve for the Fe-SMI+D-1 wire is seen to be lower than that for the Ta-7 wire at both 4.2 and 20 K. This is due to the fact that the Ta-7 wire had more carbon substitution ($x = 0.1$ in Mg(B$_{1-x}$C$_x$)$_2$) [7, 8] for boron than the Fe-SMI+D-1 wire ($x = 0.03$). At 20 K, the Fe-SMI+D-1 wire exhibits a higher $J_c$ at fields below 6 T. At 20 K and 5 T, the $J_c$ value for the Fe-SMI+D-1 wire is $7.6 \times 10^4$ A/cm$^2$, which is higher than the value of $5 \times 10^4$ A/cm$^2$ for the Ta-7 wire. It is also the highest value ever reported for MgB$_2$ wires. At 10 K, the $J_e$ values for the wires fabricated in the present study are higher than that for Nb-Ti wires at 4.2 K in the magnetic fields at which the measurements were carried out. Fig. 5-8(b) shows the $J_e$-$B$ curve for the Fe-SMI+D-1 wire, with the Ta-7 wire shown for comparison. The $J_e$ of Nb-Ti metallic superconducting wire is not shown because the paper we refereed [12] has no $J_e$ data. The $J_e$ value for the Fe-SMI+D-1 wire is about $5.3 \times 10^3$ A/cm$^2$ at 20 K and 5 T, which is almost 3 times higher than the value of $1.8 \times 10^3$ A/cm$^2$ for the Ta-7 wire. In addition, a $J_e$ value higher than $2 \times 10^4$ A/cm$^2$ could be speculated at 15 K and 5 T, which is already acceptable for applications such as magnetic resonance imaging [13] and maglev trains. Thus, IMD-processed MgB$_2$ wire is a promising candidate for such applications under liquid-helium-free conditions.
Fig. 5-8 (a) $J_c$-$B$ curves and (b) $J_e$-$B$ curves for IMD-processed MgB$_2$ wire (Fe-SMI+D-1) at different temperatures. Previously reported data for Ta-sheathed wire fabricated using SiC addition [7, 8], and $J_c$ data for Nb-Ti wires [12] are shown using dotted lines.
5.3.4 Scanning electron microscopy analysis

Fig. 5-9 (a) and (b) show SEM images of the longitudinal cross section of the MgB2 layer in the Fe-SMI wire at magnifications of 30k and 80k, respectively. High density MgB2 layer can be observed from the SEM images. A large number of bright spots can be seen against the darker background. Fig. 5-9 (c) shows EDS maps of the area seen in Fig. 5-9 (a), which indicate that the bright spots correspond to MgO. The distribution of MgO is not uniform. It can also be seen that voids with sizes of less than 100 nm (indicated by red ellipses) exist near the MgO in Fig. 5-9 (a) and (b), although the reason why the MgO and void regions are associated with each other is at present unclear. MgO is mainly considered to be the product of Mg and B2O3, and there are mainly two reasons why the B2O3 exists: one is because B powder has oxide as shown in Table 5-1, another may be due to the oxidation of nano-sized B powder during its packing in the air. These voids are thought to be the result of the poor packing of the SMI powder in the space between the Mg and the sheath. Fig. 5-9 (d) and (e) show SEM images of the longitudinal cross section of the MgB2 layer in the Fe-SMI+D-1 wire at magnifications of 30k and 80k, respectively. MgO is also seen to be present in this wire. Although from the SEM images, it is not easy to directly compare the amount of MgO in the two types of wire, the number of voids is less for the Fe-SMI+D-1 wire and the void size is smaller. This is considered to be due to the C8H10 pre-treatment, and results in a higher $J_c$ and $J_e$. Fig. 5-9 (f) and (g) show SEM images of the Ta-SMI+D wire. Although the amount of MgO appears comparable to that for the Fe-SMI and Fe-SMI+D-1 wires, almost no voids can be seen. This is consistent with our previous findings that a higher density MgB2 layer was obtained with a Ta sheath than with an Fe sheath [7, 8].
Fig. 5-9 SEM images of Fe-SMI wire at magnification of (a) 30k, and (b) 80k times, and (c) EDX maps corresponding to the area shown in (a). SEM images of Fe-SMI+D-1 wire at magnification of (d) 30k and (e) 80k times. SEM images of Ta-SMI+D wire at magnification of (f) 30k and (g) 50k times
5.3.5 Transmission electron microscopy analysis

Although the $J_c$ value is strongly dependent on the density of the MgB$_2$ layer and the level of impurities present, the nanoscale microstructure is also expected to have an important influence. Therefore, a transmission electron microscopy (TEM) analysis was carried out on the MgB$_2$ layer in the Ta-SMI+D wire that exhibited the highest $J_c$ value.

Fig. 5-10(a) shows a dark-field scanning TEM (STEM) image taken at a magnification of 25k and a camera length of 20 cm, in which the MgB$_2$ layer is seen to be uniform with a grain size of less than 100 nm. This small grain size is expected to lead to considerable flux pinning at grain boundaries. The regions labeled R1, R2, and R3 were then selected for more detailed analysis. Fig. 5-10(b) shows an image of region R1, taken at a magnification of 250k and a camera length of 20 cm. It can be seen that there are many grains with sizes less than 20 nm, as indicated by the red ellipses. Again, these are expected to act as effective flux pinning centers.

Fig. 5-10(c) and (d) show a bright-field image (300k and camera length 80 cm) and the corresponding dark-field image (300k and camera length 40 cm) of region R2, respectively. Five regions, labeled A to E, were selected for high-resolution imaging at 800K. The resulting images are shown in Fig. 5-10(e), where the insets represent electron diffraction patterns obtained by applying a fast Fourier transform (FFT) to the corresponding images. The layer was found to be mainly composed of MgB$_2$, with some MgO also being present, which is consistent with the SEM results.

Fig. 5-10(f) shows electron energy loss spectroscopy (EELS) elemental images obtained from region R3, together with a STEM-high-angle-annular-dark-field (STEM-HAADF) image for comparison. The red circles indicate MgO particles with sizes of less than 50 nm. Unreacted B particles can be also found, as indicated by the green rectangles. Since both types of particles would act as barriers to the superconducting current, it is expected that the $J_c$ value could be increased by reducing their number. The MgO particles originate mainly from the starting B powder, so their number could be reduced by refining the powder. One way of reducing the number of unreacted B particles would be to shorten the Mg diffusion distance, which could be achieved by reducing the MgB$_2$ layer thickness and fabricating multi-filament wires.
Fig. 5-10 (a) STEM dark-field image of Ta-SMI+D wire at 25k times magnification and camera length of 20 cm, (b) STEM dark-field image of region R1 in (a) at 250k times magnification and camera length of 20 cm, (c) STEM bright-field image of region R2 in (a) at 300k times magnification and camera length of 80 cm, (d) STEM dark-field image of region R2 in (a) at 300k times magnification and camera length of 80 cm, (e) high resolution images (800k) and corresponding fast Fourier transforms (FFT) of regions A to E in (c) and (d), and (f) electron energy loss spectroscopy (EELS) images of region R3 in (a).

The TEM results thus indicate that the MgB₂ layer is composed of small MgB₂ grains, mostly with sizes less than 100 nm, together with small MgO and unreacted B particles. However, similar grain sizes were also found for IMD-processed MgB₂ wires using SiC and Mg co-additives and a different type of B powder (99%, 325-mesh), for which a lower $J_c$ value of $5 \times 10^4$ A/cm² at 10 T and 4.2 K was obtained, as has been previously reported [14]. Thus, one reason for the higher $J_c$ obtained in the present study is thought to be the lower concentration of unreacted B particles in the MgB₂ layer. PIT-processed wires with much lower MgB₂ filling factors also exhibited similar grain sizes, despite the considerably lower $J_c$ values [15]. The results of the present study suggest that the most effective approach to obtaining a high $J_c$ is to produce a high-density MgB₂ layer with few voids and unreacted B particles, by suitable treatment of the wire and by ensuring a short Mg diffusion distance by producing thinner wires.
5.4 Conclusions

High-performance MgB$_2$ wires with diameters of 0.6 mm were fabricated using the IMD process. Pre-treatment of carbon-coated B powder with nanometer-sized particles using C$_8$H$_{10}$ was found to lead to an increase in the critical current. The C$_8$H$_{10}$ is thought to decrease the amount of Cl in the powder and increase the B packing density, which has a significant positive influence on the critical current.

For both Ta- and Fe-sheathed wires, the highest $J_c$ value was about 1.2 x 10$^6$ A/cm$^2$ at 4.2 K and 10 T, and the $J_e$ value was about 1 x 10$^4$ A/cm$^2$. The Fe-SMI+D-1 wire exhibited a $J_c$ of 7.6 x 10$^4$ A/cm$^2$ and a $J_e$ of 5.3 x 10$^3$ A/cm$^2$ at 20 K and 5 T, which are the highest values reported for MgB$_2$ wires to date. At 10 K, the $J_c$ value for the wires fabricated in the present study was actually higher than that for Nb-Ti wires at 4.2 K for the magnetic fields at which the measurements were carried out.

The MgB$_2$ layer in the wire that exhibited the highest $J_c$ value was found (by SEM and TEM) to be uniform and contain small grains, almost all less than 100 nm, and many less than 20 nm. Small amounts of unreacted B particles were also present in the layer. Although a similar small grain structure was found in previous IMD- and PIT-processed MgB$_2$ wires, they exhibited lower $J_c$ values. Thus, the high density of the MgB$_2$ layer and the presence of fewer and smaller unreacted B particles are considered to be the main reasons for the large critical current obtained in the present study. Further increases in the $J_c$ and $J_e$ values could be achieved by decreasing the MgO (in size and in amounts), voids and unreacted B particles. The $J_c$ value could also be increased by increasing the MgB$_2$ area fraction.

This study indicate that IMD-processed MgB$_2$ wires are promising superconductors for applications such as magnetic resonance imaging and maglev trains that can operate under liquid-helium-free conditions. The BCl$_3$ exists in SMI B powder, and the carbon-coating process by mixing the BCl$_3$, H$_2$, and CH$_4$ in RF plasma are difficult to control. These make SMI B powder not suitable for fabrication of long wires for large-scale practical applications. In chapter 6, I tried a new B powder and a new carbon-coating process.
References


[10] Private communication with Dr. James V. Marzik of Specialty Materials, Inc.


Chapter 6 Enhancement of critical current properties of MgB$_2$ wires by aromatic hydrocarbon (C$_{24}$H$_{12}$) addition

6.1 Introduction

In chapter 5, I introduced that high critical current properties can be obtained for IMD-processed MgB$_2$ wires by using nano-sized carbon-coated B powder (SMI B, particle size < 50 nm) [1-3]. The use of nano-sized B powder produced high density MgB$_2$ layer with less voids and less un-reacted B particles. This is mainly responsible for the high critical current properties we obtained. However, the SMI B powder is produced with a complex plasma spray synthesis process [4]. For this process, the BCl$_3$ gas and H$_2$ gas are injected into RF plasma to form nano-sized amorphous B powder. The BCl$_3$ is easily adsorbed on the surface of nano-sized B, which make the B powder unstable (BCl$_3$ is highly reactive with moisture) as mentioned in chapter 5. The pretreatment of SMI B powder by dimethylbenzene can decrease BCl$_3$, and thus increases the critical current properties [2, 3]. But the BCl$_3$ still exists in the B powder even after the pretreatment by dimethylbenzene. This unstable B powder increases the risk of non-uniformity of critical current properties during the fabrication process of MgB$_2$ wires for large-scale applications. Furthermore, the C-coating on B powder is through the injection of CH$_4$ into the plasma [4]. This process is very difficult to control the amount of carbon-coating. In addition, about 0.5%-1.0% B oxide exists in this B powder.

In this chapter, firstly, I changed SMI B powder for a new one. The new B powder is produced by a Turkey company. The B powder is synthesized from the following process:

$$B_2H_6 \xrightarrow{\Delta} 2B + 3H_2$$

The B powder has a particle size of less than 250 nm that is bigger than that of SMI B powder (less than 50 nm). The purity is 98.5 %, which is almost the same as the SMI B powder but no BCl$_3$ exists in the new B powder.

Secondly, I used the coronene (C$_{24}$H$_{12}$) as the carbon source. Coronene is the polycyclic aromatic hydrocarbon comprising six peri-fused benzene rings as shown in Fig. 6-1. The carbon content in the coronene molecule reaches 96 wt%. The structure of six peri-fused benzene rings has the highest symmetry of all organics except benzene. The high symmetry indicates that its
decomposed products are uniform. The coronene decomposes at about 600 °C [5]. The reaction between Mg and B for both IMD and PIT processes also occurs at about 600 °C. Therefore, we can expect that carbon atoms in coronene effectively substitute for B. Furthermore, the coronene is no toxic and abundantly exists in sedimentary rock. All these advantages suggest that coronene is a good candidate as a carbon additive for MgB₂ superconducting wires.

![Coronene molecule structure](image)

**Fig. 6-1 Molecule structure of coronene (C₂₄H₁₂)**

In this study, I applied the coronene addition to the fabrication of MgB₂ wires with both IMD and PIT processes. The critical current properties and microstructures were investigated for these wires [6].

### 6.2 Experimental details

Both IMD- and PIT-processed MgB₂ wires are fabricated with the same methods as introduced in our previous paper [7-12]. B powders for both IMD and PIT process are obtained from a Turkey company as introduced above. The coarse Mg powder with size of 100~600 μm is used for PIT process. The diameter of PIT wire is 1.0 mm. The 2%, 5%, and 10% coronene-added wires are fabricated. Undoped wires are also fabricated for comparison. All the PIT wires are heat treated at 700 °C for 1 hour.

The diameter of IMD wires is 0.6 mm. The reason of the use of small diameter for IMD wire is to decrease the Mg diffusion distance as introduced in chapter 5. The undoped, 5 mol% coronene-added, and 10 mol% SiC-added wires are fabricated. Fe tube with inner diameter of 4 mm and outer diameter of 6 mm are used as sheath. The diameters of Mg rod for all wires are 2 mm. I also changed the diameter of Mg rod to 1.8 mm for one coronene-added wire (termed C₂₄H₁₂ 5% 1) as described in chapter 5. Furthermore, several wires are also fabricated using dimethylbenzene-pretreated SMI B powder (same as in chapter 5) for comparison. All the IMD-processed MgB₂ wires are heat treated at 670 °C for 6 hours.
6.3 Results and discussion

Fig. 6-2 (a) shows an optical microscope image on transverse cross section of the PIT-processed MgB$_2$ wires (diameter: 1.0 mm). MgB$_2$ core can be found in the Fe sheath. The orange region is the high density MgB$_2$ layer, while the black region is voids. Fig. 6-2 (b) shows SEM image on the longitudinal cross section of the PIT-processed MgB$_2$ wires. The textured MgB$_2$ can be found in the wire direction, which is because the coarse Mg powders were elongated during the wire drawing. If a void is elongated in one direction, the void area in perpendicular direction could be decreased because the volume of voids that is caused by the reaction between Mg and B powders is fixed. I considered that the structure (elongated voids in wire direction) shown in Fig. 6-2(b) can enhance the critical current properties of MgB$_2$ wires because it decreases the voids in transverse cross section of the wire.

![Fig. 6-2 Transverse cross sectional image observed by optical microscope (a), and longitudinal cross sectional image observed by SEM (b) of PIT-processed MgB$_2$ wires (diameter: 1.0 mm)](image)

Fig. 6-3 (a) shows the $J_c$-$B$ curves of PIT-processed MgB$_2$ wires at 4.2 K. The undoped, 2%, 5%, and 10% coronene-added wires are compared. The highest $J_c$ values are obtained by the 10% coronene-added wires. The $J_c$ achieves $1.8 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T, which is fairly high for PIT-processed MgB$_2$ wires. As we know, the slope of $J_c$-$B$ curves can be used to estimate the amount of C substitution for B site in MgB$_2$ wires. The slope of $J_c$-$B$ curves of 2% addition is lower than that of undoped wire, while higher than that of 5% coronene-added wire. But there is no big difference between 5% and 10% addition. The less addition (undoped and 2%) show higher $J_c$ properties when we extrapolate the $J_c$-$B$ curves to low fields. We should optimize the amounts of coronene addition taking into account of the magnetic field where we use this conductor. The amount of carbon addition can be easily controlled by the amount of coronene addition, while that of carbon-coated SMI B powder is difficult to control due to the plasma process. Fig. 6-3 (b) shows the $J_c$-$B$ curves of PIT-processed MgB$_2$ wires at 4.2 K. The $J_c$ of $4.9 \times 10^3$ A/cm$^2$ at 4.2 K and
10 T was obtained by 10% coronene-added wire. The dependence of $J_c$-$B$ and $J_e$-$B$ curves on the amount of coronene addition is almost the same because the MgB$_2$ area fraction is similar for all wires due to the same wire fabrication process.

Fig. 6-3 (a) $J_c$-$B$ curves, and (b) $J_e$-$B$ curves of PIT-processed MgB$_2$ wires at 4.2 K
Fig. 6-4 shows X-ray diffraction patterns of PIT-processed MgB$_2$ wires. The amount of carbon substitution for B and $T_c$ both calculated from MgB$_2$ 110 peak according to Wilke et al’s method [13] are shown in table 6-1. The amount of carbon substitution for B is 4.5% for 5% coronene-added wires, while 4.8% for 10% coronene-added wires. This suggests that the excess coronene addition (10%) has little influence on the increase of the carbon substitution for B, which is consistent of the slopes of $J_c$-$B$ curves in Fig. 6-3. The 10% coronene-added MgB$_2$ wire has higher $J_c$ than that of 5% coronene-added wire, though they have similar amount of carbon substitution for B. This may be due to that the excess carbon in 10% coronene-added wire works as the flux pinning center to enhance the $J_c$ values. The $T_c$ values measured by resistivity method are also shown. The differences of $T_c$ values between measured and calculated are larger for undoped and 2% coronene-added wires, while smaller for 5% and 10% coronene-added wires. This may be because the impurity in B powder (<1.5%) also decreases the $T_c$. This impurity effect is not considered in Wilke et al’s method.

![X-ray diffraction patterns of PIT-processed MgB$_2$ wires](image)

Table 6-1 The properties of PIT-processed MgB$_2$ wires in this experiment

<table>
<thead>
<tr>
<th></th>
<th>Delta a (A)</th>
<th>X in Mg$(a_1\times$C$_x$)$_2$</th>
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<th>Measured $T_c$(K) by resistivity</th>
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<td>-</td>
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<td>0.048</td>
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</tbody>
</table>
Fig. 6-5 shows the SEM images of (a) undoped, (b) 2%, (c) 5%, and (d) 10% coronene-added PIT-processed MgB$_2$ wires. These images are observed in the longitudinal cross section. It is difficult to see the big difference between the undoped wires (a) and coronene-added wires (b-d).

Fig. 6-5 SEM images of (a) undoped, (b) 2%, (c) 5%, and (d) 10% coronene-added PIT-processed MgB$_2$ wires

Fig. 6-6 shows an optical microscope image on the transverse cross section of the IMD-processed MgB$_2$ wires (diameter: 0.6 mm). The MgB$_2$ layer is formed uniformly in the inner wall of Fe sheath with a hole in the wire center. The orange color of reacted layer is due to that the high density MgB$_2$ reflects light, which is similar to Fig. 2-10 in chapter 2. On the other hand, PIT-processed MgB$_2$ layer shown in Fig. 6-2 are dark or dark orange is due to the voids in MgB$_2$ layer absorb light.
Fig. 6-6 Optical microscope image on the transverse cross section of the IMD-processed MgB$_2$ wires (diameter: 0.6 mm)

Fig. 6-7 shows (a) $J_c$-$B$ curves, and (b) $J_e$-$B$ curves for IMD-processed MgB$_2$ wires fabricated in this experiment. Two coronene-added MgB$_2$ wires are shown in Fig. 6-7(a). The $J_c$ of the wires fabricated with dimethylbenzene-pretreated SMI B powder (SMI+D) are also included in the figure. The difference of two wires is a small difference of Mg rod diameter. This change of rod diameter is also introduced in chapter 5. The lower $J_c$ of SMI+D wires obtained in this chapter is due to the different heat treatment conditions. In this chapter, the wire is heat treated at 670 °C for 6 hours, while at 675 °C for 8 hours in chapter 5. The high $J_c$ value of $1.07 \times 10^5$ A/cm$^2$ at 4.2 K and 10 T is obtained for the coronene-added wire. The $J_c$ has already reached to $1.12 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T. The coronene-added wires and SMI+D wires show similar high $J_c$ and $J_e$ values. These $J_c$ and $J_e$ are all higher than those of SiC–added wires. SiC is the most popular additive for MgB$_2$ wires to date. However, the $J_c$ of SiC-added wires is about $3.3 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T in this experiment, which is a little lower than those obtained in our previous results [7-12]. Furthermore, the undoped wires show the $J_c$ of $4 \times 10^3$ A/cm$^2$ at 4.2 K and 10 T, which is also the similar level as our previous results [7-12]. The low $J_c$ values for undoped and SiC-added wires suggest that the high $J_c$ and $J_e$ obtained in this experiment is mostly due to the coronene addition. The optimization of fabrication parameters such as the amount of additive and the heat treatment condition is expected to further improve critical current properties.

This chapter is my recent work, I haven’t measure the $J_c$ and $J_e$ at 20 K. The $J_c$ and $J_e$ at 20 K should be interesting due to the similar high $J_c$ and $J_e$ as SMI B powder at 4.2 K. It is not easy to predict $J_c$ and $J_e$ values at 20 K because it is sensitive to the amount of carbon substitution for B. However, the coronene addition can control amount of carbon substitution for B which is useful to obtain high $J_e$ in both high and low fields. Furthermore, because the B powder I used in this chapter is larger than that of SMI B powder, the $J_c$ and $J_e$ are expected to be further enhanced by optimization of B powder size and addition of coronene.
Fig. 6-7 (a) $J_c$-$B$ curves, and (b) $J_e$-$B$ curves of IMD-processed MgB$_2$ wires

Fig. 6-8 shows the $J_c$ values at high magnetic fields of undoped and coronene-added MgB$_2$ wires fabricated with both IMD and PIT processes. The $J_c$-$B$ curve is still linear for all samples even at a high magnetic field of 18T. So I roughly estimated the $B_{ir}$ by extrapolating the $J_c$-$B$ curves to higher fields. In this study $B_{ir}$ is determined with a criterion of (supercurrent) $J = 100$ A/cm$^2$ in the $J_c$
measurement. The $B_{irr}$ of coronene-added IMD-processed MgB$_2$ wires has reached to 25.6 T, which is higher than the reported values for MgB$_2$ wires and tapes. The $B_{irr}$ of PIT wire reached to 22.5 T, which is similar to the 60 mol% SiC-added PIT-processed MgB$_2$ tapes [14], but the coronene I used in this experiment is only 5 mol%. This indicates that coronene addition is more effective in carbon substitution for B than SiC addition.

![Graph showing $J_c$ vs. $B$ for MgB$_2$ wires](image)

**Fig. 6-8** The $J_c$ values at high magnetic fields of undoped and coronene-added MgB$_2$ wires fabricated with both IMD and PIT processes

### 6.4 Conclusions

In this chapter, I added an aromatic hydrocarbon - coronene (C$_{24}$H$_{12}$) to MgB$_2$ wires fabricated by both IMD and PIT process. The $J_c$ of $1.8 \times 10^4$ A/cm$^2$ and $J_e$ of $4.9 \times 10^3$ A/cm$^2$ at 4.2 K and 10 T are obtained for 10 mol% coronene-added PIT-processed MgB$_2$ wires. Furthermore, a high $J_c$ of $1.07 \times 10^5$ A/cm$^2$ and a high $J_e$ of $1.12 \times 10^4$ A/cm$^2$ at 4.2 K and 10 T are obtained for coronene-added IMD-processed MgB$_2$ wires. The extrapolated $B_{irr}$ of coronene-added IMD-processed MgB$_2$ wires reached to 25.6 T at 4.2 K. These obtained values ($J_c$, $J_e$, and $B_{irr}$) are competent to the highest values reported for MgB$_2$ wires so far. The $J_c$ and $J_e$ at 20 K due to the machine time of magnet and insufficiency of helium. Because the B powder I used in this chapter is larger than that of SMI B powder, the $J_c$ and $J_e$ are expected to be further enhanced (higher than SMI or achieve to target set in chapter 1) by optimization of B powder size and addition of coronene. The coronene addition seems promising to fabricate high performance MgB$_2$ wires with low cost for large-scale practical applications.
References

Chapter 7 Summary and prospects

In this chapter, the whole thesis is summarized first, and then some topics I have done and some ongoing works are introduced, finally, prospects for the future of the IMD-processed MgB₂ wires is given.

7.1 Summary

As I introduced in the chapter 1, MgB₂ had attracted much attention for both physicist and material scientists in the first several years since its superconductivity was discovered. It is expected to be used under no-helium conditions to replace metallic superconductors that are operating in a liquid helium environment. Some companies (Hype tech in USA, Columbus in Italy, and Hitachi in Japan) have produced MgB₂ wires for sale. But the present MgB₂ can only be used in the low temperatures (4.2-20 K, obtained by liquid helium or cryocoolers), due to its low critical current properties. The application using MgB₂ for such as MRI, SMEMS, and liquid surface sensor are studied in many labs all over the world.

As we know, the $J_c$ obtained by MgB₂ film is much higher than that of the MgB₂ wire, therefore the $J_c$ could be increased if the MgB₂ wire achieves the similar microstructure to the film. Furthermore, our group developed so-called IMD process, and obtain much higher $J_c$ of MgB₂ wires than that of PIT wires. However, $J_c$ is still not so high as practical level, and $J_o$ is low either. Consequently, my work focused on enhancement of both $J_o$ and $J_c$.

The un-reacted B particles are observed in the MgB₂ layer of IMD-processed MgB₂ wires. The un-reacted B particles in MgB₂ layer are considered to be caused by the long Mg diffusion distances in IMD process. In order to decrease these un-reacted B particles, I added some amount of Mg powder in the B powder layer of IMD-processed MgB₂ wires. Consequently I developed a new method for fabricating MgB₂ wires combining IMD and PIT processes. These works were described in chapter 2. I found that Mg powder addition is effective to decrease the un-reacted B particles and to enhance the $J_c$ values. But simultaneously Mg powder addition formed some voids in MgB₂ layer and these voids decreased the $J_c$ values. After optimizing the decrease of un-reacted B particles and the decrease of voids, the high $J_c$ and $J_o$ of MgB₂ wires were obtained.

With increasing Mg powder into the B layer of IMD-processed MgB₂ wire, the Mg rod in the center of the wire should be decreased to make the balance between Mg and B. This is a new method which combined IMD and PIT processes. By this new method, the hole in the center of
IMD-processed MgB₂ wires can be decreased, simultaneously, the thickness of MgB₂ layer can be increased. Both decrease of hole and increase of MgB₂ layer thickness cause the increase of MgB₂ area fraction, thus increase the Jₑ of IMD-processed MgB₂ wires. In our experiments, the maximum Jₑ of 4.9 x 10⁴ A/cm² at 10 T and 4.2 K was obtained for M1 (6 mol% Mg addition), while the maximum Jₑ of 5.8 x 10³ A/cm² was obtained for M2 (17 mol% Mg addition). For the nano-sized B particles, the Mg powder addition could also be used to decrease the B-rich region as observed by Li et al [1, 2]. So this new method, which combined IMD and PIT processes for MgB₂ wires, can enhance Jₑ in spite of B powder size.

The multi-filamentary superconducting wires are important for practical applications. In chapter 3, we succeeded in fabricating IMD-processed 37-filamentary MgB₂ wires. SiC-added 37-filamentary MgB₂ wires show higher Jₑ value (7.6 x 10⁴ A/cm² at 4.2 K and 10 T) than the mono-filament and 7 filament wires fabricated under the same conditions. The short Mg diffusion distance of 37-filamentary IMD-processed MgB₂ wires decreases un-reacted B particles. This is the main factor giving rise to the high Jₑ values. The successful fabrication of 37-filamentary wire indicates that the IMD process can be used to fabricate MgB₂ wires for large-scale applications.

It was reported that the co-addition of SiC and ethyltoluene is effective in the PIT-processed MgB₂ wires. Accordingly, it may be also effective in the IMD-processed MgB₂ wires. In chapter 4, I used ethyltoluene and some other liquid aromatic hydrocarbons (such as toluene, and dimethylbenzene) which have similar structures to the ethyltoluene. The Jₑ properties are enhanced by the toluene and dimethylbenzene, but ethyltoluene is not so effective. This suggests that there are some differences between IMD and PIT process. The Jₑ of IMD-processed MgB₂ wire was also highly enhanced. And I first reported that IMD-wires can achieve higher Jₑ than that of PIT-wires fabricated with the same situation. I studied the mechanism of Jₑ enhancement from the microstructure. I observed the wires with SiC and/or toluene additives. I found that the SiC and toluene co-addition increases the carbon substitution for B in the MgB₂, and I also found that toluene addition make the grain size small. Furthermore, (a) the liquid hydrocarbon make the mixture the SiC and B powder uniform, (b) the adsorbed liquid aromatic hydrocarbon on the B surface prevents B from adsorbing oxide , and (c) the absorbed liquid aromatic hydrocarbon on the B surface also prevents the growth of MgB₂ grain, are all considered to contribute to the Jₑ and Jₑ enhancements. In addition, TEM observation indicates that oxide is distributed in the MgB₂ layer of SiC-added wire, which is an important discovery for the mechanism of SiC addition.

When I was doing the work mentioned above, the researchers in Ohio state university and hyper tech company used a special plasma-synthesized 2% carbon-coated B powder (Special Materials Inc., SMI powder) to fabricate thin IMD-processed MgB₂ wires (diameter: 0.55 mm). And they obtained a high Jₑ of 1.07 x 10⁵ A/cm² and a high engineering critical current density (Jₑ) of 1.67 x 10⁴ A/cm² at 4.2 K and 10 T for different samples [1]. The small diameter of the wire is considered to decrease the Mg diffusion distance, which leads to an improved reaction between Mg and B,
thus a high $J_c$ is obtained. I also tried this B powder, however, I found I can’t obtain good results as theirs. I investigated the B powder, and I found that many BCl$_3$ (source material for this B powder) exists in the B powder. Because dimethylbenzene dissolve BCl$_3$ and our experiments in chapter 2 also showed dimethylbenzene enhanced the $J_c$ of IMD-processed MgB$_2$ wires, I pre-treated SMI B powder using dimethylbenzene. I found the dimethylbenzene decreased the BCl$_3$ in B powder and then I obtained higher $J_c$ values than those of Ohio state university. For both Ta- and Fe-sheathed wires, the highest $J_c$ value was about $1.2 \times 10^5$ A/cm$^2$ at 4.2 K and 10 T, and the $J_e$ value was about $1 \times 10^4$ A/cm$^2$. Furthermore, the Fe-SMI+D-1 wire exhibited a $J_c$ of $7.6 \times 10^3$ A/cm$^2$ and a $J_e$ of $5.3 \times 10^3$ A/cm$^2$ at 20 K and 5 T, which are the highest values reported for MgB$_2$ wires to date. At 10 K, the $J_c$ value for the wires fabricated in the present study was actually higher than that for commercial Nb-Ti wires in 4.2 K for the magnetic fields at which the measurements were carried out. The researchers in Ohio state university recently reported a higher $J_c$ value [2], but their $J_c$ was calculated excluding the B-rich region where MgB$_2$ exists. Our $J_c$ value is the real $J_c$ of MgB$_2$ layer and still the highest record in the world. The detailed microstructures are also observed. These work mentioned above are introduced in chapter 5.

The carbon-coated nano-sized B powder is responsible for the high $J_c$ and $J_e$ of IMD-processed MgB$_2$ wires. However, the C-coating process of SMI B powder using plasma method is not easily carried out, thus the powder is expensive. And this B powder is unstable because BCl$_3$ exists. Therefore I tried a new B powder and used aromatic hydrocarbon coronene (C$_{24}$H$_{12}$) as the carbon source in chapter 6. Similar high $J_c$ and $J_e$ values to carbon-coated B powders in chapter 5 were obtained. The $J_e$ properties are expected to be further enhanced by optimizing the amount of heat and heat treatment conditions.

In a conclusion, there are mainly two parts of work in my Ph.D thesis. First is fabrication process of MgB$_2$ wires. Second is impurity addition. These two parts can be also divided to three stages by B powder.

First stage is chapters 2-4, which are based on the low quality B powder (325-mesh, 99%). I mainly focused on (1) search for new addition, (2) decrease of the un-reacted B by Mg addition, (3) decrease of the hole in the center, (4) increase of the MgB$_2$ area fraction, (5) development of a new method combining IMD and PIT, and (6) fabrication of 37-filamentary IMD wires.

Second stage is chapter 5, which is based on carbon-coated nano-sized B (SMI B) powder. Carbon-coated nano-sized B powder is good for enhancement of critical current properties, but it is difficult to control the amount of carbon, unstable (BCl$_3$ exists), and expensive. I used the dimethylbenzene to decrease BCl$_3$ in B powders and successfully obtained the highest $J_c$ and $J_e$ values.

Third stage is chapter 6, which is based on a new B powder, but without carbon-coating. I coated the B powder with a new hydrocarbon (C$_{12}$H$_{24}$). A high performance similar to that obtained by
dimethylbenzene-pretreated SMI B powder in chapter 5 was achieved. This work is still ongoing work. The work in this chapter is expected to be applied to fabricate the large-scale MgB₂ with low cost for practical applications.

I think the works performed in my PHD thesis have contained some new results for MgB₂ wires, but there are still many unfinished works which should be further studied. Below I want to introduce some ongoing work (7.2), and then give a prospect for MgB₂ wires (7.3).
7.2 Some ongoing topics

The following works are mainly carried out by my colleagues. Some are partly finished (7.2.1) and some are un-finished (7.2.2 and 7.2.3). I introduce them here because these works are related to the work of my PHD thesis. Furthermore, these works are important for the development of the high performance MgB₂ wires for practical applications, and need to be continued.

7.2.1 The comparison of mechanical properties for IMD- and PIT-processed MgB₂ wires

In this work, mechanical properties in magnetic fields of MgB₂ mono-core wires fabricated with both IMD and PIT processes were investigated. Both IMD and PIT wires are fabricated with 10 mol% SiC-added 325-mesh B powder by using the method introduced in chapter 4. The detail of the work is published [3]. Here I just give a simple introduction:

Fig. 7-1 shows the apparatus used to measure $I_c$ under uniaxial tension. A 40 mm long sample was prepared. Both ends (10 mm each) were soldered to current terminals of the test apparatus. A pair of voltage taps with 10 mm separation were soldered on the specimen. The stress value was deduced from the tensile load, which was measured by a load cell, and divided by the whole cross-sectional area of the sample. The strain value was deduced from the displacement, which was measured by a clip-on gauge, and divided by the initial length of the specimen.

Fig. 7-1 Photograph (left) and schematic illustration (right) of apparatus to measure $I_c$ versus uniaxial tension
Fig. 7-2 shows the tensile strain ($\varepsilon$) dependence of $I_c$ for IMD-MgB$_2$ and PIT-MgB$_2$ wires at 10 T, 4.2 K. Solid markers indicate $I_c$ measured at fixed strain. Open markers indicate $I_c$ measured at zero stress which is to check the reversibility of $I_c$. The strain did not go back to zero when the stress was released to zero because of the plastic deformation of the wire. The obtained $I_c$-$\varepsilon$ relations of both wires are similar in shape. $I_c$ increased linearly and reversibly with increasing tensile strain up to the reversible limit (irreversible strain, $\varepsilon_{irr}$), at which the maximum $I_c$ value was observed. $I_c$ deteriorated irreversibly at $\varepsilon > \varepsilon_{irr}$. The irreversible strain $\varepsilon_{irr}$ values were 0.67% and 0.54% for IMD and PIT wires, respectively. The inset of Fig. 7-2 shows the reversible region ($\varepsilon < \varepsilon_{irr}$) of $I_c$-$\varepsilon$ normalized by $I_{c0}$ ($I_c$ at zero strain). Each $(I_c/I_{c0})$-$\varepsilon$ plot can be fitted with a linear function. The slope values of each function correspond to the strain sensitivity. The deduced strain sensitivity values are 0.14 and 0.21 for IMD and PIT wires, respectively.

![Image](image1)

<table>
<thead>
<tr>
<th>$\varepsilon_{irr}$</th>
<th>$d(I_c/I_{c0})/d\varepsilon$</th>
</tr>
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<tbody>
<tr>
<td>IMD</td>
<td>0.67%</td>
</tr>
<tr>
<td>PIT</td>
<td>0.54%</td>
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<tr>
<td></td>
<td>0.143</td>
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<td>0.213</td>
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Fig. 7-3 shows the apparatus used to measure $I_c$ under transverse compression. Both ends (10 mm each) of the 40 mm long sample were soldered to current terminals of the test apparatus. A pair of voltage taps with 10 mm separation was soldered. The width of the pressure block, which is made of GFRP (glass-fiber-reinforced plastics), is 3 mm. The compressive stress was calculated using the pressure block width and the cross-sectional area of the wire.

Fig. 7-4 shows transverse compressive stress ($\sigma_t$) dependence of normalized $I_c$ ($(I_c/I_{c0})$-$\sigma_t$) for IMD and PIT wires at 10 T, 4.2 K. Solid and open markers indicate $I_c$ at fixed (loaded) strain and at stress-released condition, respectively. $I_c$ remained the initial value and was reversible up to a
certain threshold stress. $I_c$ deterioration of IMD-MgB$_2$ wire started at the transverse compressive stress of 206 MPa, whereas PIT-MgB$_2$ wire $I_c$ at 160 MPa.

This experiment was carried out only at 4.2 K. IMD-processed MgB$_2$ wires showed better mechanical properties in magnetic fields than those of PIT-processed MgB$_2$ wires. The other temperatures (10-20 K), sheath materials, and the number of filaments should be considered in the future work.

Fig. 7-3 Schematic illustration (left) and photo (right) of apparatus to measure $I_c$ versus transverse compression

Fig. 7-4 Normalized $I_c$ as a function of transverse compressive stress (both IMD and PIT are fabricated with 325-mesh B with 10 mol% SiC addition as the method introduced in chapter 4)
7.2.2 Strain measurement of IMD-processed MgB$_2$ wires by synchrotron radiation at SPring-8

The superconductive properties are affected by external strain. $J_c$ under a stress of superconducting wire was investigated in 7.2.1. When a distortion is added to a superconducting wire, the strain condition is different depending on the internal structure and the manufacturing method of wire. Therefore, it is necessary to observe directly the distortion of internal superconductor in the superconducting wire. A lattice strain measurements of MgB$_2$ wire were performed by diffraction method at the BL22XU of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2013B1573 and 2012B1435). The BL28B2 diffractometer and the experimental layout are shown in Fig. 7-5 (a) and (b), respectively. The relations between a load strain and the lattice strain of a measured ex situ PIT-processed MgB$_2$ wires are shown in Fig. 7-6. The MgB$_2$ crystal showed elastic distortion behavior for the loading force. We haven’t finished the measurement of IMD-processed MgB$_2$ wires due to the short machine time, and we will apply the next machine time to do it.

Fig. 7-5 (a) The diffractometer and (b) experiment layout

Fig. 7-6 The relations of a load strain and the lattice strain
7.2.3 Reaction observation of IMD-processed MgB$_2$ wires during the heat treatment by XRD in Spring-8

In this research, we used the strong XRD to observe the reaction process of IMD-processed MgB$_2$ wires during the heat treatment. We measured the XRD pattern twice per second. The experiment is carried out with the station 3 of beam BL22XU in the spring-8 (Under the shared use program of Japan Atomic Energy Agency Facility (JAEA Proposal No. 2013A-E22 and 2013B-E20, JASRI Proposal No. 2013A3789 and 2013B3782)). Fig. 7-7 shows (a) the experimental equipment, (b) magnified image, and (c) wire furnace. The sample was sealed in a silica tube filled with Ar gas, which is similar to the real heat treatment process. The photon energy of XRD is 30 keV, and the beam size is 0.5 x 0.2 mm. The detecting image is a 2-D diffraction pattern, as shown in Fig. 7-8(a). The calculated 1-D diffraction pattern data are shown in Fig. 7-8 (b). MgB$_2$ can be found in the heat treatment process from the obtained data, while there is only Mg peak for no heat treatment sample. This experiment gives the direct information of the MgB$_2$ formation reaction during the heat treatment. We can expect to enhance the critical current properties by controlling the microstructure of MgB$_2$ based on the information. The experiment is not yet completed due to limited machine time. We will continue the measurement when we have enough machine time.

Fig. 7-7 (a) Experimental equipment, (b) magnified image, and (c) wire furnace
Fig. 7-8 (a) 2-D data of XRD diffraction, and (b) 1-D data of XRD calculated from (a)
7.3 Prospects

As introduced in Chapter 1, “low cost” is the most important advantage of MgB₂ superconducting wires. PIT-processed MgB₂ wires have been applied to the prototype of MRI. However, both the product cost and the operating cost are still high, which is mainly because the low critical current properties need the high operation conditions (low temperature and/or low field). IMD-processed MgB₂ wires have showed much better critical current properties than PIT-processed wires as introduced in this thesis. We also found that IMD-processed MgB₂ wires have better mechanical properties. However, the critical current properties of IMD MgB₂ wires are still below the practical level. In order to develop high performance IMD-processed MgB₂ wires feasible for large-scale applications, the first task is the enhancement of critical current properties (especially the critical current properties at 20 K and 5 T). Meanwhile, some other properties (such as mechanical properties, AC loss) of the IMD-processed MgB₂ wires should also be considered.

I consider that the future research of IMD-processed MgB₂ wires should focus on the following topics:

1. B and impurity addition

   (a) B powder: B powder is crucial for the critical current properties of IMD-processed MgB₂ wires. The main reason for the high $J_c$ in 7- and 19- filamentary wires obtained by our group should be attributed to the high quality B powder. The high $J_c$ and $J_e$ values recently obtained by both Ohio state university [1, 2] and our group are also attributed to the carbon-coated high quality nanosized B powders (chapter 5). The high $J_c$ properties of both IMD- and PIT-processed MgB₂ wires obtained in chapter 6 are mainly due to the C₂H₂ addition, but it should also be attributed to the high quality B powder. To date, we haven’t understood what kind of B powder is useful for the high $J_c$ properties of MgB₂. Investigation of the influence of B powder on $J_c$ properties is a difficult but very important work.

   (b) Carbon-containing impurity addition: carbon-containing impurity addition is widely used for MgB₂ wires. Carbon substitution for B enhances $J_c$ only in high magnetic fields. But $J_c$ in low field decreases because carbon decreases the connectivity of MgB₂ grains. The control of carbon substitution for B to increase $J_c$ in high magnetic fields with less decrease of $J_c$ in low fields needs to be studied.

   (c) No carbon addition: there are thousands of reports on impurity additives but no one have good reproducibility except for carbon source addition. However, this doesn’t mean that there is no effective source other than carbon.
2. Study of Mg diffusion mechanism in IMD process

To date, there are no reports on the diffusion mechanism of Mg in IMD-processed MgB\textsubscript{2} wires because the diffusion mechanism is not easy to investigate. The following parameters affecting the Mg diffusion should be considered:

(a) The Mg rod diameter, B layer thickness, B packing density, and the sheath materials.

(b) The B powder quality and B powder size.

(c) Heat treatment conditions (temperature and time).

The understanding of the diffusion mechanism is useful to improve the reaction between Mg and B, to control the microstructure (grain size, and texture) of MgB\textsubscript{2}, and to increase the MgB\textsubscript{2} area fraction in the wire.

3. Properties important for large-scale applications

The purpose of MgB\textsubscript{2} wire development is practical applications with low cost. The first task is the enhancement of the critical current properties without the increase of fabrication cost, meanwhile, other properties should also be considered.

(a) Sheath materials: no reaction with Mg and B, good thermal and electric conductivity, easy for the wire fabrication, low cost...

(b) Electrical properties such as AC loss

(c) Mechanical properties: strain and stress effects were measured only at 4.2 K for monofilamentary wire in 7.2.1. Other temperatures (10-20 K), sheath materials, and the number of filament should be considered.

 Sometimes luck is more important than sense, which is just like that superconductivity of MgB\textsubscript{2} was discovered in 2001 [4], 47 years later since its preparation was first reported [5].
References

Publications

Scientific papers

[1] Ye S J, Matsumoto A, Togano K and Kumakura H 2011 Physica C 471 1133 Enhancement of the critical current density of internal Mg diffusion processed MgB₂ wires by the addition of both SiC and liquid aromatic hydrocarbon


Presentations

(1) 葉術軍、松本 明善、戸叶 一正、熊倉 浩明、「拡散法 MgB2 線材における不純物添加効果」、2011 年度春季低温工学・超電導学会、2011/05/18-2011/05/20、つくば、日本、講演番号：2P-20. (Poster)

(2) Ye S J, Song M, Matsumoto A, Togano K, Takeuchi M, Kumakura H, Teranishi R, Kiyoshi T, "Comparison of SiC and/or toluene additives to the critical current density of internal Mg diffusion-processed MgB2 wires", the 24rd International Symposium on Superconductivity (ISS2011), 2011/10/24-2011/10/26, Tokyo, Japan, Program number: WTP-42. (Poster)

(3) 葉術軍、松本 明善、戸叶 一正、熊倉 浩明、寺西 亮、木吉 司、「内部拡散法（IMD）による 19、37 芯 MgB2 線材の作製」、2011 年度秋季低温工学・超電導学会、2011/11/09-2011/11/11、金沢、日本、講演番号：2P-p17. (Poster)


(7) 葉術軍、松本 明善、戸叶 一正、熊倉 浩明、寺西 亮、木吉 司、「内部 Mg 拡散法 MgB2 線材における MgB2 の層厚と臨界電流特性」、2012 年度秋季低温工学・超電導学会、2011/11/09-2011/11/11、岩手、日本、講演番号：2P-p02. (Poster)

(9) 葉術軍、松本 明善、張 雲超、戸叶 一正、熊倉 浩明、「内部拡散法による MgB₂ 線材の臨界電流特性及び微細組織」、2013 年度春季低温工学・超電導学会、2013/5/13-2013/5/15、東京、日本、講演番号：2C-a02. (Oral)


(12) 葉術軍、松本 明善、戸叶 一正、大村孝仁、熊倉 浩明、「IMD 法と PIT 法をミックスした方法による高臨界電流密度 MgB₂ 線材の作製」、2013 年度秋季低温工学・超電導学会、2013/12/4-2013/12/6、東京、日本、講演番号：2B-a04. (Oral)

Patent

(1) 熊倉 浩明、松本 明善、葉術軍、MgB₂ 超伝導体の製造方法および MgB₂ 超伝導体、日本特許、出願番号：2013-259711