Enhancement of connectivity and flux pinning in MgB2 superconducting bulks and wires

Lin Lu
University of Wollongong

Follow this and additional works at: https://ro.uow.edu.au/theses

Recommended Citation
NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.
Enhancement of Connectivity and Flux Pinning in MgB$_2$ Superconducting Bulks and Wires

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

Master of Engineering by Research

From the

UNIVERSITY OF WOLLONGONG

By

Lin Lu

Institute for Superconducting and Electronic Materials

2009
DECLARATION

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

Lin Lu
2009
ACKNOWLEDGMENTS

I would like to express my deep gratitude to my supervisors, Prof. S. X. Dou, Dr. R. Zen, for their continuous academic guidance, encouragement, and support during my three years of Master study in the Institute for Superconducting and Electronic Materials at the University of Wollongong.

I thank Dr. T. Silver for her kind help in proofreading and correcting the English in the manuscripts of my journal articles and this thesis.

I would also like to express my appreciation to Prof. H. K. Liu, Prof. X. L. Wang, Dr. J.L. Wang, Dr. J. Horvat, Dr. A. Pan, Dr. S. Zhou and Dr. K. Konstantinov for their contributions to measurements and for useful discussions and valuable suggestions.

My special thanks to all my colleagues at ISEM including, Mrs. Y. Zhang, Mr. W. X. Li and all the members and technicians at the Faculty of Engineering, especially Mr. R. Kinnell, Mr. G. Tillman, and Mr. N. Mackie, for their friendly help and assistance in using the facilities.

I would also like to acknowledge the Australian Government for providing my APA scholarship and the Research Student Centre at the University of Wollongong who managed my scholarship for their enthusiastic support.

Finally I wish to thank my parents, parents-in-law, and my husband for their patience and support. In particular, without my husband’s encouragement and support, I really would not have been able to continue my academic work. I also believe that my lovely son has given me good luck, as well as a lot of fun.
# Table of Content

Abstract .................................................................................. 1

Chapter 1: introduction ....................................................... 4

  1.1 Background .................................................................. 4
  1.2 Objective of the thesis ................................................. 5
  1.3 References ................................................................. 7

Chapter 2: Literature Review on MgB₂

Superconductor ...................................................................... 8

  2.1. History of Superconductors ...................................... 8
      2.1.1. The Low Temperature Superconductors (LTS) .... 9
      2.1.2. The High Temperature Superconductors (HTS) .... 9
  2.2 The Discovery of MgB₂ .............................................. 10
  2.3 Crystal and Electronic Structure of MgB₂ .................. 11
  2.4 Superconducting Properties of MgB₂ ......................... 13
      2.4.1 Critical Temperature, \( T_c \)............................... 14
      2.4.2 Critical Current Density, \( J_c \), and Flux Pinning ... 14
      2.4.3 The resistivity of MgB₂ ................................. 16
  2.5 Electron Phonon Coupling in the Superconductivity of MgB₂ ................................................. 17
  2.6 Preparation Method .................................................... 18
      2.6.1 Bulk MgB₂ Superconductor ............................ 18
Chapter 3: Synthesis and Characteristics of Highly Dense MgB₂ Bulks

3.1 Highly Dense MgB₂ Bulks

3.1.1 Introduction

3.1.2 Experimental

3.1.3 Results and Discussion
Chapter 4: Significant improvement of critical current density of \textit{in situ} MgB$_2$ by excess Mg addition

4.1 Excess Mg addition MgB$_2$ bulks

4.1.1 Introduction

4.1.2 Experimental

4.1.3 Results and Discussion

4.1.4 Conclusion

4.2 Excess Mg addition MgB$_2$/Fe wires

4.2.1 Introduction

4.2.2 Experimental procedure

4.2.3 Results and discussion

4.2.4 Conclusions

4.3 References

Chapter 5: conclusions

Publications

VI
List of Tables

Table 3.2.1  Physical properties of pure and SiC-MgB$_2$ composite samples………60

Table 4.1.1  Comparison of full width at half maximum (FWHM), critical temperature ($T_c$), and $J_c$ (10$^4$ A/cm$^2$) at 20 K, 2 T and at 5 K, 4 T for normal MgB$_2$ and 10% excess Mg MgB$_2$ sintered at different temperatures……………………………………..84

Table 4.2.1  Comparison of full width at half maximum (FWHM), irreversibility field ($H_{irr}$) and transport $J_c$ (10$^4$ A/cm$^2$) at 20 K, 4 T and at 10 K, 8T for normal MgB$_2$ and 10 at% excess Mg MgB$_2$ wires sintered at different temperatures………………………………97
## List of Figures

| Figure 2.1.1 | Evolution of critical temperature, \( T_c \), with time……………………………8 |
| Figure 2.3.1 | Crystal structure of MgB\(_2\) [10]……………………………………………………12 |
| Figure 2.6.1 | Phase diagram of Mg + B [84]……………………………………………………….19 |
| Figure 2.6.2 | Powder-in-tube (PIT) process for the in-situ and ex-situ methods….22 |
| Figure 2.6.3 | MgB\(_2\) wire segments made from 100 \( \mu \)m diameter boron filaments [90]………………………………………………………. 25 |
| Figure 2.7.1 | Theoretical concept of the “in-situ” reaction of Mg and B [111]……….30 |
| Figure 2.8.1 | The \( J_c \) field dependence of MgB\(_2\) samples doped with 10 wt% of different SiC powders, as well as a pure reference sample, at the temperatures of 5, 20, and 30 K [124]……………………………………32 |
| Figure 3.1.1 | (a) XRD patterns; (b) \( a, c \) lattice parameters………………………………………50 |
| Figure 3.1.2 | Normalized resistivity and normalized susceptibility (inset) vs. temperature around \( T_c \)…………………………………………………………………………51 |
| Figure 3.1.3 | (upper panel) \( T_c \) of samples based on AC susceptibility from magnetic measurements and from transport measurements from the start of the transition and the zero resistance point; (lower panel) percentage of theoretical density and actual density (number labels)………………………………………………………52 |
| Figure 3.1.4 | SEM images of 100% diffusion sample (left) and 100% in-situ sample (right)………………………………………………………………………………………….52 |
| Figure 3.1.5 | Resistivity vs. temperature from 30 to 300 K. The inset shows the \( A_F \) values (effective cross-sectional areas) for the different samples…..53 |
| Figure 3.1.6 | Magnetic \( J_c \) versus field at 5 K, 20 K and 30 K …………………….54 |
| Figure 3.1.7 | Normalized resistance versus temperature at fields from 0 to 8.7 T..55 |
| Figure 3.1.8 | Upper critical field (\( H_{c2} \)) and irreversibility field (\( H_{irr} \)) as functions of the temperature. The inset shows \( H_{c2} \) and \( H_{irr} \) as functions of the normalized temperature…………………………….56 |
Figure 3.2.1 XRD patterns of pure MgB$_2$ and 10wt% SiC doped MgB$_2$ samples that were diffusion reacted at 850$^\circ$C for 10 hrs. 

Figure 3.2.2 Magnetic $J_c$ versus field at 5 K, 20 K, and 30 K for pure and nano-SiC doped samples.

Figure 3.2.3 Upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$) as functions of the temperature. The inset shows the resistivity of these samples as a function of temperature.

Figure 3.2.4 (a) Plots of the normalized lattice changes for MgB$_2$ and SiC, and the thermal strain in the matrix during cooling from 1123 K to 0 K. (b) The thermal expansion coefficient ($\alpha$) for MgB$_2$ and SiC as a function of temperature. Plots are based on data from [32-35].

Figure 3.2.5 Bright field TEM images for the two-phase composite: (a) and (c) overview at different magnifications; (b) and (d) interface between the SiC particles and the MgB$_2$ matrix. The insets in (b) are selected area electron diffraction (SAED) patterns for the MgB$_2$ and SiC sides of the interface. The arrows point to defects.

Figure 3.2.6 Normalized ambient Raman spectra of samples sintered at 850$^\circ$C for 10 hrs.

Figure 3.2.7 The normalized $J_c/T$ at $H = 0.1$ T versus reduced temperature ($T/T_c$) and fitting of normalized $J_c(T)$ with various pinning models for pure MgB$_2$, SiC + MgB$_2$ composite, and C substituted Mg ($B_{0.9}C_{0.1}$)$_2$ samples.

Figure 4.1.1 (a) $a$- and $c$-lattice parameters versus sintering temperature; (b) the MgO content versus sintering temperature.

Figure 4.1.2 The magnetic critical current density ($J_c$) at 20 K versus magnetic field for 10% excess Mg and normal MgB$_2$ sintered at different temperatures. The inset shows transport $J_c$ at 20 K versus magnetic field for 10% excess Mg and normal MgB$_2$ wires sintered at 750$^\circ$C.

Figure 4.1.3 Irreversibility field ($H_{irr}$, round symbols) and upper critical field ($H_{c2}$, square symbols) as a function of temperature for (a) normal and (b) 10 at% Mg excess MgB$_2$ bulk samples sintered in the temperature range from 650$^\circ$C to 950$^\circ$C.

Figure 4.1.4 Irreversibility field ($H_{irr}$, open symbols) and upper critical field ($H_{c2}$, closed symbols) as a function of temperature for pure and 10 % Mg excess MgB$_2$ samples sintered at 650$^\circ$C. The inset on the upper right shows resistivity as a function of temperature from 300 down to 20 K in self-field, and the inset on the lower left.
the temperature dependence of the resistivity from 16 to 40 K at different magnetic fields (0, 1, 2, 3, 4, 5, 6, 7, 8 and 7 T)........90

**Figure 4.1.5** Upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$) as a function of temperature for normal and 10 wt% Mg excess MgB$_2$ samples sintered at 750°C. The inset is the normal-state resistivity as a function of temperature for normal and 10% Mg excess MgB$_2$ samples processed at 750°C....91

**Figure 4.1.6** Normal-state resistivity as a function of temperature for (a) normal and (b) 10 at% Mg excess MgB$_2$ samples sintered within the temperature range of 650°C to 950°C.........................93

**Figure 4.2.1** (a) PC and DC transport $J_c$ at 4.2 K, 10 K and 20 K for samples treated at 800°C; (b) PC transport $J_c$ at 10 K and 20 K for all samples, and (c) DC transport $J_c$ at 20 K for samples treated at 600°C for 1 hour or at 700°C and 800°C for 30 min.................................100

**Figure 4.2.2** X-ray diffraction patterns of the superconducting cores of Fe sheathed wires sintered at temperatures from 600 to 900°C: (a) normal stoichiometric MgB$_2$ samples and (b) 10 at% Mg excess samples..............................................102

**Figure 4.2.3** X-ray diffraction patterns of bulk samples sintered at temperatures from 650 to 950°C: (a) normal stoichiometric MgB$_2$ samples and (b) 10 at% Mg excess samples..............................................103

**Figure 4.2.4** SEM images of normal samples sintered at (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C.................................105

**Figure 4.2.5** SEM images of 10 at% Mg excess samples sintered at (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C.......................106
ABSTRACT

The objective of this work is to improve the connectivity and flux pinning and hence to enhance the critical current density of MgB$_2$ superconductor by the development of following processes and techniques: densification and use of excess Mg addition, substitution and inclusion by doping with nano C, nano-SiC or carbon nanotube (CNT) and BN.

Firstly, a new, direct Mg-diffusion method to synthesize highly dense pure MgB$_2$ bulks has been developed, in which pressed boron bulks are separately packed in sealed iron tubes that have been filled with magnesium powder and then sintered at high temperature over a long period. The influence of the bulk density on the superconducting properties of MgB$_2$ has been investigated through synthesizing bulks with different densities, using a combination of diffusion and the in-situ method. This method is easily applicable to the fabrication of highly dense MgB$_2$ bulks and tape-shaped samples. It was found that the connectivity was significantly improved as the effective area (AF) varied from 0.2 (conventional in-situ) to 0.42 (diffusion), hence the self-field critical current density, $J_c$, is significantly improved compared with conventional porous MgB$_2$ bulks made by the in-situ method. A sample reacted at 850 °C for 10 hrs exhibited $J_c$ of 1.2 MA/cm$^2$ at 20 K in self-field.
Secondly, a novel artificial pinning centre method has been developed by using thermal strain to induce defects in MgB$_2$ superconductors. Strain engineering has been used previously to modify material properties in ferroelectric, superconducting, and ferromagnetic thin films$^8$. The advantage of strain engineering is that it can achieve unexpected enhancement in certain properties, for example, it can increase the ferroelectric critical temperature, $T_c$, by 300 to 500$^\circ$C, with a minimum detrimental effect on the intrinsic properties of the material. Strain engineering has been largely applied to materials in thin film form, where the strain is generated as a result of lattice mismatch between the substrate and component film, or between layers in multilayer structures. The residual thermal stress/strain has been observed in dense SiC-MgB$_2$ superconductor composites prepared by the diffusion method. The thermal strain caused by the different thermal expansion coefficients ($\alpha$) between the MgB$_2$ and SiC phases is responsible for the significant improvement in the critical current, $J_c$, the irreversibility field, $H_{irr}$, and the upper critical field, $H_{c2}$, in the SiC-MgB$_2$ composite. In contrast to the common practice of improving the $J_c$ and $H_{c2}$ of MgB$_2$ through chemical substitution, SiC-MgB$_2$ composite shows only a small drop in $T_c$ and little increase in resistivity but exhibits a significant improvement over the $J_c$ and $H_{c2}$ of conventional MgB$_2$ due to the advantage of residual thermal strains. The present findings open up a new direction for manipulation of material properties through strain engineering in materials in various forms.
Another part of the work in this thesis was on MgB$_2$ bulks and wires that were fabricated by in-situ solid state reaction and the powder-in-tube method, respectively. The effects of excess Mg on the structure and physical properties, such as the lattice parameters, the critical temperature ($T_c$), the critical current ($J_c$), the irreversibility field ($H_{irr}$), and the upper critical field ($H_{c2}$), have been detailed. It was found that $J_c$, $H_{irr}$, and $H_{c2}$ were significantly enhanced for Mg excess samples. All these properties were highly sensitive to the processing temperature for the Mg excess samples, while there was only a weak dependence on processing temperature for normal ones. For the bulks, the $T_c$ variation for the 10% Mg excess sample was 1.6 K (36.3 K to 37.9 K) when the sintering temperature was changed from 650$^\circ$C to 850$^\circ$C, while it only varied by 0.5 K (37.2 K to 37.7 K) for the normal sample. The low field $J_c$ for the 10% Mg excess samples sintered at 750$^\circ$C increased by a factor of 3, compared to that for the normal MgB$_2$ sample, while the $H_{c2}$ for the 10% Mg excess samples sintered at 650$^\circ$C reached 8.7 T at 25 K, compared to 6.6 T for the normal sample. Rietveld refinement x-ray diffraction (XRD) analysis showed that the MgO content was reduced in 10% excess Mg samples, leading to an increase in the effective cross section of the superconductor.

MgB$_2$ / Fe wires with 10 at% excess Mg produced by in-situ powder-in-tube processing were compared with normal stoichiometric MgB$_2$ / Fe wires prepared by the same method. It was found that the critical current ($J_c$) and the irreversibility field ($H_{irr}$) were significantly enhanced for MgB$_2$ / Fe wires with excess Mg. The transport
$J_c$ for 10 at% Mg excess samples sintered at 800°C, measured in fields up to 14 T, increased by a factor of 2 compared to that for the normal MgB$_2$ wires. The best $J_c$ results for a 10 at% Mg excess sample were obtained by heating the sample for 1 h at 600 °C, resulting in $J_c$ for a field of 8 T and a temperature of 10 K that reached $3 \times 10^4$ A/cm$^2$. A detailed analysis of the effects of excess Mg on the microstructures, the $J_c$, and the $H_{irr}$ of MgB$_2$/Fe wires is presented in this thesis.