

2008

Effect of the starting boron powder on the superconducting properties of MgB

Xun Xu
University of Wollongong

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

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: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. 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.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Recommended Citation

Xu, Xun, Effect of the starting boron powder on the superconducting properties of MgB, PhD thesis, Institute of Superconducting and Electronic Materials, University of Wollongong, 2008.
<http://ro.uow.edu.au/theses/353>

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.

Effect of the Starting Boron Powder on the Superconducting Properties of MgB₂

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

DOCTOR OF PHILOSOPHY

From the

UNIVERSITY OF WOLLONGONG

By

XUN XU, B. Eng., M. Eng.

Institute for Superconducting and Electronic Materials

2008

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.

Xun Xu

2008

ACKNOWLEDGMENTS

I would like to express my deep gratitude to my supervisors, Prof. S. X. Dou, Dr. M. J. Qin, and Dr. J. H. Kim, for their continuous academic guidance, encouragement, and support during my three years of PhD 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. Horvat, Dr. J. H. Jiang, Dr. G. Peleckis, Dr. Y. Zhao, and Dr. K. Konstantinov for their contributions to measurements and for useful discussions and valuable suggestions.

This work would not have been completed without the help of Dr. S. K. Chen and Dr. W. K. Yeoh from the University of Cambridge, Mr. M. Tomsic and Mr. M. Rindfleish from Hyper Tech, USA, Dr. S. Choi, Dr. T. Kiyoshi, Dr. T. Nakane, and H. Kumakura from the National Institute for Materials Science (NIMS), Japan, Miss J. H. Lee and Prof. H. W. Park from the Korea University of Technology and Education, Mr. D. Z. Liu from TangShan Weihao Magnesium Powder Co., Ltd., and Prof. P. R. Munroe from the University of New South Wales for their great collaboration.

My special thanks to all my colleagues at ISEM including Mr. D. P. Chen, Mrs. Y. Zhang, Dr. S. Zhou, Mr. W. X. Li, Dr. Z. Rong, M. S. Park, S. H. Ng, S. Y. Chew, J. S. Park, 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 Research Council for providing my APAI 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 wife for their patience and support. In particular, without my wife's encouragement, 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. I consecrate this thesis to my wonderful mother, who passed away at the beginning of this year. I wish she could understand my hard work and forgive any mistakes I have made.

Table of Content

| | |
|---|-----------|
| ABSTRACT | 1 |
| CHAPTER 1: INTRODUCTION..... | 4 |
| 1.1 BACKGROUND..... | 4 |
| 1.2 MOTIVATION AND AIMS | 6 |
| 1.3 THESIS ORGANIZATION:..... | 8 |
| 1.4 REFERENCES | 11 |
| CHAPTER 2: LITERATURE REVIEW ON POLYCRYSTALLINE MGB₂ SUPERCONDUCTOR | 13 |
| 2.1 INTRODUCTION | 13 |
| 2.2 “PURE” POLYCRYSTALLINE MGB ₂ | 20 |
| 2.2.1. <i>Discovery of MgB₂</i> | 20 |
| 2.2.2. <i>Fabrication of MgB₂ conductors</i> | 21 |
| 2.2.3 <i>Wire and tape preparation</i> | 23 |
| 2.2.4 <i>Phase transformation and crystal structure of MgB₂</i> | 24 |
| 2.2.5 <i>Formation of MgO within MgB₂</i> | 26 |
| 2.2.6 <i>Superconductivity and microstructures of MgB₂</i> | 30 |
| 2.2.7 <i>Comparison between wire and tape</i> | 37 |
| 2.2.8 <i>Comparison between in situ and ex situ processing</i> | 42 |
| 2.3 EFFECT OF BORON POWDER PURITY ON MGB ₂ | 44 |
| 2.3.1 <i>Characteristics of Boron (B)</i> | 44 |
| 2.3.2 <i>Market trends</i> | 44 |
| 2.3.3 <i>Influence of Boron Precursor Powders</i> | 45 |
| 2.3.4 <i>Purification of low-grade boron powders -- acid leaching process</i> | 47 |
| 2.3.5 <i>Mechanical alloying effect on MgB₂</i> | 57 |
| 2.4 EFFECTS OF MG PRECURSOR POWDER ON MGB ₂ SUPERCONDUCTIVITY | 64 |
| 2.4.1 <i>Mg powder</i> | 64 |
| 2.4.2 <i>MgH₂ powder instead of Mg powder</i> | 66 |
| 2.5 CHEMICAL DOPING EFFECTS | 68 |
| 2.5.1 <i>Dual reaction model and dopant categories</i> | 68 |
| 2.5.2 <i>Carbohydrate Doping</i> | 70 |
| 2.6 LARGE-SCALE APPLICATION WITH MGB ₂ | 71 |

| | |
|---|------------|
| 2.7 REFERENCES | 75 |
| CHAPTER 3: EXPERIMENTAL TECHNIQUES | 86 |
| 3.1 SAMPLE PREPARATION AND PROCESSING CONDITIONS | 86 |
| 3.1.1 Planetary Ball-milling | 86 |
| 3.1.2 Preparation of bulk and wire samples | 88 |
| 3.2 SAMPLE CHARACTERIZATION | 89 |
| 3.2.1 Particle Size Analysis | 89 |
| 3.2.2 X-ray Diffraction (XRD) | 90 |
| 3.2.3 Differential Thermal Analysis (DTA) | 91 |
| 3.2.4 Scanning electron microscopy (SEM), Energy dispersive X-ray spectrometry (EDS), and Transmission electron microscopy (TEM) | 93 |
| 3.2.5 Brunauer-Emmett-Teller (BET) | 93 |
| 3.2.6 Measurements of T_c , J_c , H_{c2} , H_{irr} | 94 |
| 3.3 REFERENCES | 99 |
| CHAPTER 4: DIFFERENT MEDIA EFFECT FOR THE MGB₂ BULK SAMPLE BY BALL MILLED HIGH PURITY BORON..... | 101 |
| 4.1 INTRODUCTION | 101 |
| 4.2 SAMPLE PREPARATIONS | 103 |
| 4.3 PHASE INFORMATION AND LATTICE PROPERTIES | 104 |
| 4.4 SEM STUDIES | 107 |
| 4.5 INFERENCE ON J_c AND T_c | 109 |
| 4.6 SUMMARY | 112 |
| 4.7 REFERENCES | 113 |
| CHAPTER 5: INFLUENCE OF BALL-MILLED LOW PURITY BORON POWDER ON THE SUPERCONDUCTIVITY OF MGB₂ BULK SAMPLE..... | 115 |
| 5.1 MOTIVATION AND SCOPE | 115 |
| 5.2 EXPERIMENTAL DETAIL | 116 |
| 5.3 PHASE INFORMATION AND MICROSTRUCTURE OF 96% BORON | 117 |
| 5.4 PHASE INFORMATION AND LATTICE PARAMETERS | 119 |
| 5.5 COMPARISON OF T_c , J_c , AND PINNING FORCE | 122 |
| 5.6 SUMMARY | 125 |
| 5.7 REFERENCES | 126 |

CHAPTER 6: THE PHASE TRANSFORMATION AND SUPERCONDUCTING PROPERTIES OF MgB_2 BY DIFFERENT BORON SOURCE 127

| | |
|--|-----|
| 6.1 OPEN WINDOW FOR LOW PURITY BORON | 127 |
| 6.2 EXPERIMENTAL DETAIL..... | 129 |
| 6.3 SEM STUDIES FOR DIFFERENT BORON POWDER..... | 131 |
| 6.4 PHASE TRANSFORMATION OF MgB_2 SAMPLE WITH DIFFERENT SOURCE | 133 |
| 6.5 PARTICLE SIZE DISTRIBUTIONS OF BALL-MILLED 96% BORON POWDER | 135 |
| 6.6 PHASE INFORMATION AND LATTICE PARAMETERS | 137 |
| 6.7 MGO EFFECT (TWO KNIFE-EDGES) | 139 |
| 6.8 RESISTIVITY AND CONNECTIVITY EFFECT..... | 141 |
| 6.9 COMPARISON OF T_c , J_c , AND PINNING FORCE STRENGTH..... | 143 |
| 6.10 UPPER CRITICAL FIELD AND IRREVERSIBILITY FIELD FROM TRANSPORT MEASUREMENT | 146 |
| 6.11 CONCLUSION..... | 148 |
| 6.12 REFERENCES | 149 |

CHAPTER 7: FURTHER STUDY OF TRANSPORT CURRENT DENSITY AND GRAIN CONNECTIVITY IN MgB_2/Fe WIRE MADE FROM BALL-MILLED LOW PURITY BORON..... 150

| | |
|---|-----|
| 7.1 WHY NEED WIRE RESULT FOR COMPARISON..... | 150 |
| 7.2 SAMPLE PREPARATIONS..... | 153 |
| 7.3 PARTICLE SIZE DISTRIBUTIONS | 155 |
| 7.4 SEM STUDIES | 157 |
| 7.5 TRANSPORT CRITICAL CURRENT (J_{ct}) | 159 |
| 7.6 RELATION BETWEEN THE TRANSITION TEMPERATURE AND RESISTIVITY | 161 |
| 7.7 UPPER CRITICAL FIELD AND IRREVERSIBILITY FIELD FROM TRANSPORT MEASUREMENT | 163 |
| 7.8 CONCLUSION..... | 165 |
| 7.9 REFERENCES | 166 |

CHAPTER 8: THE DOPING EFFECTS OF OXYGEN-FREE PYRENE ON THE SUPERCONDUCTIVITY OF MgB_2 WIRES... 167

| | |
|---|-----|
| 8.1 PRESENTMENT THE DOPING EFFECTS WITH OXYGEN-FREE CARBON SOURCE | 167 |
| 8.2 SIMPLY SAMPLE PREPARATION ROUTE | 170 |

| | |
|---|------------|
| 8.3 PHASE INFORMATION AND LATTICE PROPERTIES..... | 171 |
| 8.4 TRANSPORT CRITICAL CURRENT (J_c) | 175 |
| 8.5 POWER-LAW RELATIONSHIP BETWEEN J_c AND N-VALUE | 177 |
| 8.6 SUMMARY | 179 |
| 8.7 REFERENCES | 180 |
| CHAPTER 9: PROPERTIES OF CARBON SPHERES DOPED MGB₂ WIRE BY LOW PURITY BORON POWDER..... | 181 |
| 9.1 POSSIBILITY OF CARBON SOURCE DOPING EFFECTS IN LOW PURITY BORON | 181 |
| 9.2 CARBON SPHERES PREPARATIONS..... | 183 |
| 9.3 MGB ₂ WIRE PREPARATIONS | 184 |
| 9.4 COMPARISON BETWEEN MGB ₂ WIRES BY HIGH AND LOW PURITY BORON WITHOUT DOPING | 185 |
| 9.5 CARBON SPHERES DOPED MGB ₂ WIRES BY THE LOW PURITY BORON | 190 |
| 9.6 CONCLUSION | 197 |
| 9.7 REFERENCES | 198 |
| CHAPTER 10: CONCLUSIONS AND FURTHER WORK..... | 200 |
| 10.1 CONCLUSION..... | 200 |
| 10.2 SUGGESTIONS FOR FURTHER WORK | 203 |
| PUBLICATIONS | 205 |

List of Figures

| | | |
|--------------------|---|----|
| Figure 2.1 | History of superconductor development with time..... | 14 |
| Figure 2.2 | Crystal structure of MgB_2 , $a = 3.086 \text{ \AA}$ and $c = 3.524 \text{ \AA}$ [26]..... | 20 |
| Figure 2.3 | The powder-in-tube (PIT) process for the <i>in situ</i> and <i>ex situ</i> methods [38]..... | 22 |
| Figure 2.4 | SEM images of (a) Mg and (b) B powders [24]..... | 23 |
| Figure 2.5 | Differential Thermal Analysis (DTA) for MgB_2/Fe wire..... | 24 |
| Figure 2.6 | X-ray diffraction (XRD) patterns for un-doped MgB_2/Fe wires sintered at different temperatures. The XRD was performed on the ground MgB_2 cores [23]..... | 25 |
| Figure 2.7 | (a) Lattice parameters and (b) weight fractions of MgB_2 and MgO for samples made at different sintering temperatures [23]..... | 27 |
| Figure 2.8 | Standard Gibbs free energy (ΔG) of $2\text{Mg(s)} + \text{O}_2(\text{g}) = 2\text{MgO(s)}$; $4\text{Mg(s)} + \text{B}_2\text{O}_3(\text{l}) = 3\text{MgO(s)} + \text{MgB}_2(\text{s})$; and $\text{Mg(s)} + 2\text{B(s)} = \text{MgB}_2(\text{s})$ as a function of temperature..... | 29 |
| Figure 2.9 | Lattice strain versus average grain size (from measured results) as a function of sintering temperature [23]..... | 31 |
| Figure 2.10 | Field emission gun-scanning electron microscopy (FEG-SEM) images of core surface for samples sintered at 650°C ((a) and (b)), 800°C ((c) and (d)), and 1000°C ((e) and (d)) [24]..... | 32 |
| Figure 2.11 | Critical current density (J_c) of all MgB_2/Fe wire samples at 4.2 K and 10 T. Magnetic fields were applied parallel to the wire axis of the MgB_2 wire. Inset shows the $J_c(\text{B})$ of all samples as a function of sintering temperature [24]..... | 33 |
| Figure 2.12 | Resistivity (ρ) of MgB_2/Fe wires as a function of temperature for three samples sintered at different temperatures. Transport measurements for ρ were done using a standard ac four probe method. The inset shows an enlargement of the temperature range around T_c [24]..... | 34 |
| Figure 2.13 | FEG-SEM images of polished core surfaces for samples sintered at (a) 650°C , (b) 800°C , and (c) 1000°C [24]..... | 36 |

| | | |
|---------------------|--|----|
| Figure 2.14 | Temperature dependence of irreversibility field (H_{irr}) and upper critical field (H_{c2}) for MgB ₂ /Fe wires sintered at various sintering temperatures for 30 min[24]..... | 37 |
| Figure 2.15 | (a) Transport J_c for round wires and flat tapes at 4.2 K. Inset figure shows the J_c behaviour of referenced wire samples at 4.2 K and 10 T as a function of sintering temperature. (b) Kramer plot (F_K), $J_c^{1/2} \times B^{1/4}$ vs. B , for round wires and flat tapes at 4.2 K [23]..... | 39 |
| Figure 2.16 | SEM images of polished cross-sections for round wire ((a) and (b)) and flat tape ((c) and (d)) [64]..... | 40 |
| Figure 2.17 | SEM image of cross-section of a flat tape. There were cracks in the middle of the core (indicated by white arrows) [64]..... | 41 |
| Figure 2.18 | $J_c(B)$ behaviour of <i>in situ</i> processed flat tape compared to commercial and modified <i>ex situ</i> processed flat tapes [64]..... | 42 |
| Figure 2.19 | FEG-SEM images of samples (a) C98, (b) C99, (c) A9597, and (d) A9999 [67]..... | 46 |
| Figure 2.20 | Magnetic critical current densities versus applied magnetic field at 6 K and 20 K [67]..... | 47 |
| Figure 2.21 | Acid leaching process [68]..... | 49 |
| Figure 2.22 | BET results for different B powders [68]..... | 50 |
| Figure 2.23 | SEM images of different Boron powders [68]..... | 51 |
| Figure 2.24a | X-ray powder diffraction patterns of MgB ₂ samples made from pure 99% B powder [68]..... | 52 |
| Figure 2.24b | X-ray powder diffraction patterns of MgB ₂ samples made from 96% B powder [68]..... | 53 |
| Figure 2.24c | X-ray powder diffraction patterns of MgB ₂ samples made from purified 92% B powder [68]..... | 54 |
| Figure 2.25 | J_c of samples made from different B powders [68]..... | 56 |
| Figure 2.26 | Granulometry for different ball milled MgB ₂ powders: (a) 2 h, distribution peaks 3/30 μ m; (b) 3 h, distribution peaks 1.5/10 μ m; (c) 14 h, distribution peaks 1/7 μ m; and (d) 100 h, distribution peak 1 μ m [69]..... | 58 |
| Figure 2.27 | Transport and inductive measurements of the irreversibility field H_{irr} , for MgB ₂ /Fe tapes prepared with commercial and ball milled powders[69]..... | 59 |

| | | |
|--------------------|--|-----|
| Figure 2.28 | Dependence of the critical current density on the parallel field for CuNi/Nb double-sheathed tapes with nanocarbon-doped MA precursor annealed at different temperatures [96]..... | 63 |
| Figure 2.29 | SEM images of the magnesium powders with a particle size of (a) 44 μm (Alfa Aesar), (b) 12–17 μm (Tangshan Weihao), (c) 4–6 μm (Tangshan Weihao), and (d) boron powder with 95–97% purity from Tangshan Weihao [103]..... | 65 |
| Figure 2.30 | Comparison of critical current density, J_c , as a function of magnetic field at 5 and 20 K for samples W5, W6, and W7 annealed at 700 °C for 30 min [103]..... | 66 |
| Figure 2.31 | The ASG MRI 0.5 T cryogenic-free magnet [184]..... | 72 |
| Figure 2.32 | The ASG MRI 0.5 T cryogenic-free magnet [184]..... | 73 |
| Figure 3.1 | planetary Ball-milling working principles [8]..... | 87 |
| Figure 3.2 | Principle about determination of the powder particle size [10]..... | 89 |
| Figure 3.3 | X-ray diffract meter in θ - 2θ configuration taken from reference [11] | 90 |
| Figure 3.4 | Schematic illustration of a DTA cell [14] | 92 |
| Figure 3.5 | A typical DTA result of a sample with endothermic and exothermic reactions [14]..... | 92 |
| Figure 3.6 | Schematic diagram of magnetic hysteresis loop of a Superconductor showing the width of the magnetic hysteresis loop ΔM [18]..... | 96 |
| Figure 3.7 | Magnetic hysteresis measured on a bulk MgB_2 at 6K up to 7T. The flux jumping is due to thermomagnetic instabilities causing a sudden dissipative re-arrangement of magnetic flux lines [19]..... | 97 |
| Figure 4.1 | The X-ray diffraction patterns for the MgB_2 samples made with and without ball milling in various media..... | 105 |
| Figure 4.2 | SEM images for the MgB_2 samples..... | 107 |
| Figure 4.3 | The magnetic critical current density J_c as a function of field for the MgB_2 samples..... | 109 |
| Figure 4.4 | The T_c curves for the MgB_2 samples..... | 110 |
| Figure 5.1 | X-ray diffraction patterns for the different B powders..... | 117 |

| | | |
|-------------------|---|-----|
| Figure 5.2 | SEM images of the different B powders..... | 118 |
| Figure 5.3 | X-ray diffraction patterns for MgB ₂ samples made with the different B powders..... | 119 |
| Figure 5.4 | The magnetic critical current density J_c as a function of field for the MgB ₂ samples..... | 122 |
| Figure 5.5 | Normalized volume pinning force ($F_p/F_{p,max}$) as a function of field at 20K for the MgB ₂ samples..... | 123 |
| Figure 6.1 | Scanning electron microscope (SEM) images of (a) 96% B and (b) 99% B. Inset shows a high magnification image of 96% B..... | 131 |
| Figure 6.2 | Scanning electron microscope (SEM) images for (a) B96, (b) BM4B96, (c) BM8B96, and (d) BM12B96..... | 132 |
| Figure 6.3 | Differential Thermal Analysis (DTA) for MgB ₂ with different B powders..... | 133 |
| Figure 6.4 | Particle size distributions for (a) B96, (b) BM4B96, (c) BM8B96, and (d) BM12B96..... | 135 |
| Figure 6.5 | (a) a - and c -axis lattice parameters, (b) c/a , (c) full width at half maximum (FWHM) of the (110) peak, and (d) lattice strain of MgB ₂ samples using different B..... | 138 |
| Figure 6.6 | Relative intensity, MgO(220) / MgB ₂ (110) + MgB ₂ (102), as a function of ball-milling time. The inset shows the relative pinning force as a function of field for the different samples..... | 139 |
| Figure 6.7 | The magnetic critical current density (J_c) for all MgB ₂ samples as a function of external magnetic field at 5 and 20 K..... | 143 |
| Figure 6.8 | Kramer plot (F_k) of the pinning force, $J_c^{1/2} \times B^{1/4}$, for all samples at 20 K..... | 144 |
| Figure 6.9 | Temperature dependence of irreversibility field (H_{irr}) and upper critical field (H_{c2}) for all samples with different ball-milling times..... | 146 |
| Figure 7.1 | Particle size distributions for (a) as-supplied and (b) ball-milled boron powders..... | 155 |
| Figure 7.2 | Scanning electron microscope (SEM) images at two magnifications for (top) wire sample prepared from as-supplied boron, and (bottom) wire sample prepared from ball-milled boron. All samples were sintered at 700°C for 30 minutes..... | 157 |

| | | |
|-------------------|--|-----|
| Figure 7.3 | Transport critical current density (J_{ct}) for all MgB ₂ wires as a function of external magnetic field at 4.2 K..... | 159 |
| Figure 7.4 | The correlations between (a) the transition temperature (T_c) and the residual resistivity ratio (RRR), and (b) the critical temperature (T_c) and the normalized resistivity (ρ_{norm})..... | 162 |
| Figure 7.5 | Temperature dependence of (a) the upper critical field (B_{c2}) and (b) the irreversibility field (B_{irr}) for MgB ₂ wires as a function of sintering temperature..... | 163 |
| Figure 8.1 | (a) a -axis lattice parameter, (b) lattice strain, and (c) fraction of MgO/Mg for pristine MgB ₂ and MgB ₂ + C ₁₆ H ₁₀ /Fe wires as a function of amount of the pyrene. All wire samples were sintered at 650°C for 30 min. The solid line show a linear fit to the data..... | 172 |
| Figure 8.2 | (a) a -axis lattice parameter, (b) c -axis lattice parameter, and (c) actual amount of carbon (C) substitution (x) in the composition of Mg(B _{1-x} C _x) ₂ for pristine MgB ₂ and MgB ₂ + 10wt% C ₁₆ H ₁₀ /Fe wires as a function of sintering temperature. The wire samples were sintered at 600°C for 4 hours, 620°C for 1 hour, 650°C for 30 min, 700°C for 30 min, and 800°C for 30 min, respectively. The solid line show a linear fit to the data..... | 173 |
| Figure 8.3 | Transport critical current density (J_c) of pristine MgB ₂ and MgB ₂ + 10wt% C ₁₆ H ₁₀ /Fe wires as a function of applied magnetic field and sintering temperature..... | 175 |
| Figure 8.4 | Power-law relationship between J_c and n -value, $n \propto J_c^m$ | 177 |
| Figure 9.1 | SEM images of the submicron-sized carbon spheres prepared by hydrothermal treatment of glucose solution at 180°C..... | 183 |
| Figure 9.2 | XRD patterns of the pure MgB ₂ samples prepared by sintering at different temperatures..... | 185 |
| Figure 9.3 | Magnetic AC susceptibility as a function of temperature for the pure samples sintered at different temperatures..... | 187 |
| Figure 9.4 | Critical current density, J_{cm} , as a function of magnetic field at 5 and 20 K for the undoped samples sintered at different temperatures. The J_{cm} of the sample (700°C) prepared from high purity (99%) amorphous boron is included as reference..... | 188 |
| Figure 9.5 | Temperature dependence of H_{c2} and H_{irr} for the pure samples sintered at 650 and 800°C, and the sample prepared from 99% amorphous boron sintered at 700°C..... | 190 |

| | | |
|-------------------|---|-----|
| Figure 9.6 | The (002) and (110) XRD reflections of the pure, 5 and 10 wt.% CS doped samples. The heat treatment temperature for these samples is 800°C..... | 192 |
| Figure 9.7 | Critical current density, J_{cm} , as a function of magnetic field at 5 and 20 K for the pure and CS doped samples..... | 193 |
| Figure 9.8 | The H_{c2} and H_{irr} of the pure and CS doped samples sintered at 800°C as a function of reduced temperature (T/T_c)..... | 194 |
| Figure 9.9 | Normalized flux pinning force as a function of reduced magnetic field at 20 K for the pure and CS doped samples sintered at 800°C. The solids lines corresponds to the function $h^p(1-h)^q$ with different p and q values representing different pinning mechanisms..... | 195 |

List of Tables

| | | |
|------------------|--|-----|
| Table 2.1 | Source, form, and purity of the different boron powders with their particle size distribution [67]..... | 45 |
| Table 2.2 | Nominal purity, impurities, grain size, and crystallinity of boron precursor powders from different suppliers [69]..... | 60 |
| Table 2.3 | Synthesis parameters, structural analysis by x-ray diffraction, microstructure analysis by SEM-EDX and superconducting properties of hot pressed bulk samples [69]..... | 62 |
| Table 2.4 | Synthesis parameters, microstructure analysis by SEM-EDX and superconducting properties of tapes [69] | 54 |
| Table 2.5 | Ranking of dopants by Dual Reaction Model [Dou, 2007-EUCAS].... | 69 |
| Table 4.1 | The full-width at half maximum (FWHM) of 3 main peak positions and lattice parameters for the MgB ₂ samples made with and without ball milling in various media..... | 104 |
| Table 5.1 | The lattice constants and structural features for the MgB ₂ samples made with the different B powders..... | 121 |
| Table 6.1 | The measured resistivity values, residual resistivity ratios (RRR), and active cross-sectional area fraction (A _F) for MgB ₂ with different ball-milling times..... | 141 |
| Table 7.1 | The measured resistivity values, residual resistivity ratios (RRR), active cross-sectional area fractions (A _F), critical temperatures (T _c), and lattice strain for MgB ₂ wire made from ball-milled boron and from as-supplied boron under comparable sintering conditions..... | 158 |
| Table 9.1 | Summaries of characteristic data for the pure and CS doped MgB ₂ samples sintered at 800°C..... | 192 |

Abstract

The effect of the properties of the starting boron powders on the superconducting properties of MgB_2 has been studied. Low grade boron powders are attractive because of their low cost, but produced lower surface reactivity and larger particle size than high purity (99%) amorphous boron powder, indicating that the low grade powders cannot be used to achieve the same superconducting properties as those of samples made from pure 99% boron powder. However, the low purity boron powders can be improved by using simple physical and chemical processes, leading to enhanced magnetic critical current density, J_c . In order to get high performance MgB_2 , it is obviously important to control the phase composition and microstructure of the boron starting powders and the solid state reaction conditions.

Ball milling is an effective method to reduce the boron particle size, so, the effects of ball milling boron powders in different media, such as acetone, ethanol, and toluene, on the superconducting properties of MgB_2 needed to be considered and studied. It was observed that toluene was the most effective medium of them all for enhancing J_c . J_c was estimated to be $5 \times 10^3 \text{ A cm}^{-2}$ at 8 T and 5 K for a sample that was ball milled in toluene. This value is much higher than that of the pure MgB_2 reference sample that was not ball milled, by a factor of 20. It was considered that ball milling B using toluene leads to smaller MgB_2 grains, resulting in enhanced J_c at low operating temperatures and high fields.

MgB_2 samples were prepared using as-supplied commercial 96% boron with strong crystalline phase and the same 96% boron (B) after ball milling. The effects of the properties of the starting B powder on the superconductivity were evaluated. It was

observed that samples using ball-milled 96% B, in comparison with the reference sample made from the as-supplied 96% B, were characterized by small grain size and enhanced magnetic critical current density (J_c), which reached $2 \times 10^3 \text{ A cm}^{-2}$ at 5 K and 8 T. The improved pinning seen in these samples seems to be caused by enhanced grain boundary pinning at high field. MgB_2 samples were also prepared by using 96% boron powder with strong crystalline phase that had been ball milled for various times. Based on Rowell connectivity analysis, when the ball-milling time increased, the connectivity factor, described as the active cross-sectional area fraction (A_F), was decreased. This implies that the inter-grain connectivity became worse. These properties could lead to poor J_c in low field. However, the pinning force strength of samples using ball-milled 96% B is larger than that of the reference sample using as-supplied commercial 96% B powder. These results accompany enhanced irreversibility (H_{irr}) and upper critical fields (H_{c2}).

Furthermore, the magnetic field dependence of the transport critical current density (J_{ct}) and the grain connectivity of MgB_2/Fe wires fabricated from ball-milled boron have been investigated in detail, and strong correlations have been found, as evidenced by differences in grain size, critical transition temperature, and resistivity. It was observed that the samples fabricated by ball milling had relatively small grain sizes, resulting in a weaker field dependence of the J_{ct} in the high field region. On the other hand, the ball-milled boron was associated with poor connectivity between adjacent grains. It is clearly shown that the observed reduction in low field J_{ct} is related to the reduction in the superconducting area fraction that is reflected by the connectivity factor. Even though high temperature sintering could always compensate for the degradation of the J_{ct} in the low field region, the subsequent grain growth in this case was mainly responsible for the degradation of J_{ct} in the high field region. The strong correlation

between the grain size and the connectivity can change the field dependence of the J_{ct} , and both these factors are primarily affected by the sintering temperature and by the presence and extent of ball milling.

In the MgB_2 field, chemical doping is the most popular way to improve the superconductor properties. It has been reported that significantly enhanced critical current density in MgB_2 superconductor could be easily obtained by doping with a hydrocarbon, highly active pyrene ($C_{16}H_{10}$), while using a sintering temperature as low as $600^\circ C$. The processing advantages of the $C_{16}H_{10}$ additive include production of a highly active carbon (C) source, an increased level of disorder, and the introduction of small grain size, resulting in enhancement of J_c .

Using the same concept, low purity boron powders were used to fabricate pure and submicron-sized carbon sphere doped MgB_2 superconductor. The boron powders used showed low reactivity towards MgB_2 formation, as compared to high purity (99%) amorphous boron, which might result from the larger grain size and the existence of crystalline boron or boron oxide in the former. However, the samples prepared from this boron powder showed comparable J_c values at 20 K and in low field (<1 T) to those from a sample prepared from 99% amorphous boron. Doping submicron-sized carbon spheres successfully introduced carbon substitution for boron, and so improved the H_{c2} , H_{irr} , and in-field J_c properties of the MgB_2 .