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Improvement of critical current density in MgB2 by optimizing process parameters and chemical doping

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This thesis is presented as part of the requirements for the award of the Degree of Doctor of Philosophy of the University of Wollongong

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DECLARATION

I, Yun Zhang, declare that this thesis, submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials (ISEM), Faculty of Engineering, University of Wollongong, Australia, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for a qualification at any other academic institution.

Yun Zhang

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ABSTRACT

The discovery of superconductivity in MgB_2 in January 2001 has triggered enormous interest around the world. MgB_2 has evolved as a promising superconductor for the next generation of superconductor applications, due to not only its higher critical temperature (T_c = 39 K), low material cost, and good weak-link tolerance, but also its rich multiple-band structure. However, several issues exist that urgently need to be solved, such as its low upper critical field (H_{c2}) and rapid decrease in critical current density (J_c) under magnetic field compared to Nb-based superconductors. High $J_c(H)$ performance is crucial for the application of this material in the so-called "strong electrical application" field. Therefore, the objective of this thesis is to increase J_c of bulk polycrystalline MgB_2 via studying the influence of the boron precursor powder and the nominal Mg/B mixing ratio and efforts to further enhance J_c by doping with two types of sources: carbon sources (such as SiC and sucrose) and oxygen sources (such as TiO_2/SiO_2 and processing atmospheres with different oxygen content).

The control of the boron powder is one of most promising methods to enhance J_c at high fields without significant decrease of the self-field J_c. The particle size, purity, and form of the starting boron powders play an important role in the superconducting properties of MgB_2. It has been proved the precursor B powder is very important to critical current density of MgB_2. In terms of the influence of boron precursor on the superconducting properties of MgB_2, J_c values for MgB_2 made from ball-milled high purity boron powders with crystalline phase are at least two times higher than for a comparable MgB_2 sample made from ball-milled amorphous boron powder and a factor of 40 higher

than typical values of standard MgB_2 samples. The possible mechanism proposed to account for this difference is H_{c2} enhancement caused by the increased disorder.

Nano-particle SiC is a very effective dopant to improve the in-field J_c of MgB_2. However, J_c at lower field become lower than the undoped one. It would be desirable to maintain a high low-field J_c while improve the high field J_c. In order to solve this issue, the influence of Mg content was investigated in a series of undoped and SiC-doped MgB_2 samples with systematic variation of the nominal Mg/B ratio (x:2). It has been found that in the undoped MgB_2 samples J_c increases with x to a maximum value at x = 1.1 and then decreases. The higher J_c at x = 1.1 is attributed to the better connectivity caused by smaller amounts of impurities. In the SiC-doped samples, it has been found that the sample with x = 1.15 exhibits the best J_c performance for all fields from 0 – 8.5 T, including the self-field, and its T_c is higher than for the sample with x = 1. The enhancement of J_c is attributed to the improved connectivity and the increased disorder. The optimized Mg/B ratio (1.15:2) also diminishes the interband scattering caused by the Mg or B vacancies and, in turn, increases T_c.

Carbonhydrates such as sucrose can decompose at high emperature. The resulting carbon from the decomposition can be used as carbon source to dope into MgB_2. This kind of carbon is very reactive and can be incorporated into MgB_2 easier. A comprehensive study of the effects of carbohydrate doping on the superconductivity of MgB_2 has been conducted. Doping with sucrose at varying rates and annealing temperatures results in an optimal J_c value in $MgB_{2-x}C_x$ at x = 0.2 and 850 ^oC. At 5 K and 6 T, the x = 0.2 sample shows one order of magnitude improvement compared to pure sample. It has been found that sucrose doping causes a small depression in T_c and

high resistivity, while H_{c2} performance is improved. The reason for the enhancement of H_{c2} is likely to be increased disorder caused by C substitution for B and/or diffusion of C atoms in the MgB_2 lattice as interstitial atoms.

TiO_2/SiO_2 additions lead to improved J_c values. J_c values are the highest at the doping ratio of 10 wt% at 5 K and 20 K, and at the doping ratio of 5 wt% at 30 K, when the sintering temperature is fixed at 750 ^oC. When the doping ratio is fixed at 5 wt%, the sample with the sintering temperature of 750 ^oC has the best J_c for 5 K and 20 K, while the sample with the sintering temperature of 850 ^oC exhibits the highest J_c at 30 K. In addition, it has been found that the addition of TiO_2/SiO_2 nanoparticles results in a small depression in T_c, while the H_{c2} and irreversibility field (H_{irr}) performances are improved. The enhancement of H_{c2} and H_{irr} can be attributed to the existence of precipitates induced by the TiO_2/SiO_2 doping.

The effect of processing atmosphere on microstructure and superconducting properties was studied for MgB_2 samples made using the *in situ* reaction technique under argon atmosphere with three different purities, ultra-high, high, and welding grade. The critical temperature, T_c, decreases by 0.5 K while the FWHM, the resistivity and the amount of MgO show an increase in the welding Ar processed sample. The J_c, H_{irr} and H_{c2} for the welding Ar processed sample are improved in comparison with the samples treated in ultra-high and high purity argon. Transmission electron microscope (TEM) examination revealed that the sample processed in welding grade argon possessed small grains, a high density of defects, and larger crystalline strains, which act as effective pinning centres. These results verify the dual reaction model where the MgB_2 formation and the reaction between oxygen and precursor take place simultaneously, resulting in

an optimal doping effect. The $J_c(H)$ behaviour for samples treated at 800^oC for 60 hours in the sealed Fe tube shows little difference among the three different Ar atmospheres. The optimal J_c and flux pinning properties in MgB_2 can be achieved by using readily available and economical welding grade Ar as the protective atmosphere instead of using ultra-high or high purity Ar. The effects of the sintering time on the superconductivity of MgB_2 with sintering in the welding grade Ar atmosphere have been investigated. The sample sintered for 30 min exhibits the highest J_c at high fields. The reason can be attributed to the improved connectivity and the increased H_{c2}.

Overall, the works in this thesis are mainly on material process and characterization. I have studied many factors such as precursor powder, process parameters, dopants that have strong effects on J_c. The results are useful for future MgB_2 fabrications.

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