2008

Effect of Addition of TiO2/SiO2 Nanoparticles on Hc2 and Hirr in MgB2 Bulks

Y. Zhang
University of Wollongong

Saeid Soltanian
University of Kurdistan, Iran, saeid@uow.edu.au

Y. Zhao
University of Wollongong, yue_zhao@uow.edu.au

S. Zhou
University of Wollongong, sihai_zhou@uow.edu.au

S. X. Dou
Univeristy of Wollongong, shi@uow.edu.au

Effect of Addition of TiO_2/SiO_2 Nanoparticles on H_{c2} and H_{irr} in MgB_2 Bulks

Yun Zhang[1], Saeid Soltanian[2], Yue Zhao[1], SiHai Zhou[1], ShiXue Dou[1]

[1] Institute for Superconducting and Electronic Materials, University of Wollongong, Northfields Ave. Wollongong, NSW 2522, Australia
Email: yz268@uow.edu.au

[2] Department of Physics and Research Center for Nanotechnology, University of Kurdistan, PO Box 416, Sanandaj, Iran
Email: SSoltanian@uok.ac.ir

Abstract— In this paper, MgB_2 bulks were prepared with doped TiO_2 nanoparticles surface-modified by 5-10% SiO_2. Quantitative X-ray diffraction (XRD) analysis was performed to obtain the weight fraction of impurities using the Rietveld method. The effects of addition of TiO_2/SiO_2 nanoparticles on the critical temperature (T_c), the upper critical field (H_{c2}), and the irreversibility field (H_{irr}) as a function of doping rates at 750°C are reported. It has been found that the addition of TiO_2/SiO_2 nanoparticles resulted in small depressions in T_c, while the H_{c2} and H_{irr} performances were improved due to TiO_2/SiO_2 nanoparticle doping.

Keywords-upper critical field; irreversibility field; doping; magnesium diboride; TiO_2/SiO_2

I. INTRODUCTION

The superconductivity at 39K discovered in MgB_2 [1] has aroused much interest in practical applications. Its low cost, high critical temperature (T_c), freedom from weak-links [2], [3], and multiple energy gaps [4], [5], [6] offer the possibility for application in magnets and various electronic applications. However, the significant potential of MgB_2 for applications is limited by poor flux pinning and the relatively low upper critical field (H_{c2}) and irreversibility field (H_{irr}). So far, substitution and addition have been widely used to improve the critical current density (J_c), H_{c2}, and H_{irr}. Large numbers of elements have been studied for either J_c or H_{c2} and H_{irr} improvement by substitution. Currently, only Al replacing Mg and C replacing B have been possible for higher doping level [7], [8], [9], [10]. Other substituting dopants, such as the transition metal elements (Fe, Y, Ti, Zr) in the Mg sub-lattice are limited to very low concentration [11], [12], [13], [14]. Compound additions, such as SiC [8], B_4C [15], Y_2O_3 [16], SiO_2 [17], [18], and TiO_2 [19] have exhibited positive effects on J_c, H_{c2} and H_{irr}. Therefore, adding nanoparticles which cause compositional and nanostructural changes in MgB_2, has been proved to be an effective way to enhance the performance of MgB_2.

Among these dopants, the authors' group found that J_c could be improved by TiO_2 doping under low magnetic fields, while SiO_2 doping played a role under high magnetic fields. Perner et al. [17] have reported that the optimum SiO_2 doping level of around 2 wt.% improved the flux pinning ability of MgB_2. In our recent study of the effect of atmosphere on the J_c of MgB_2, it was suggested that the particular amount of O_2 might play a very important role [20]. This is another reason why metal oxides, in particular, have attracted attention rather than other compounds. These results motivated us to add TiO_2 and SiO_2 nanoparticles into MgB_2 simultaneously. In order to make homogeneous samples by co-doping, TiO_2 nanoparticles coated by 5-10% SiO_2 were used. In this paper, we performed a systematic study of H_{c2} and H_{irr} with different doping levels for samples sintered at the temperature of 750ºC, and we have found an enhancement of the H_{c2} and H_{irr} for MgB_2 samples with 5-10wt% TiO_2/SiO_2 doping, along with a small depression in T_c.

II. EXPERIMENTAL

MgB2 bulks were prepared by the *in-situ* method. Powders of Mg (99%), amorphous B (99%) were used as starting materials.TiO2 nanoparticles (15 nm) with a purity of 99.7% and surface modified by 5-10% SiO_2 were used as the dopant. The doping ratios were 0, 5, and 10 wt% and the sintering temperature was 750°C. Amorphous boron powder was dried for 9 days in oven at 120°C before mixing with the Mg powders. The powders were well ground and pressed into stainless steel tubes with 10mm outer diameter and 7mm inside diameter, using a 5 ton press. This packing process was carried out in air. The samples were heated from room temperature to the sintering temperatures in a tube furnace under Ar atmosphere at ambient pressure, and kept at the sintering temperature for 1 hour. The samples were then furnace cooled to room temperature. The obtained MgB2 samples were examined by a Phillips PW1730 X-ray power diffractometer with CuKα radiation (λ=1.5418Å). The X-ray diffraction (XRD) patterns were collected over a 2θ range from 20° to 80° with a step size of 0.02°. The quantitative phase analysis was carried out based on the XRD patterns. Magnetic measurement

TABLE 1 Measured data for un-doped and doped MgB2 samples

samples	*sintering conditions*	*MgO at%*	*Mg_2si at%*	*ρ_{40K} ($\mu\Omega$cm)*	*ρ_{300K} ($\mu\Omega$cm)*	*$\Delta\rho$ ($\mu\Omega$cm)*	*RRR*	*FWHM(110) (^{o})*	*T_c (K)*	*J_{C020K} (A/cm^2)*
Un-doped MgB_2	750°C 1H	5.7		30.1	79.7	49.6	2.7	0.44	37.8	$5.177x10^5$
MgB_2 + 5% TiO_2/SiO_2	750°C 1H	17	1	122	215	93.1	1.8	0.52	36.2	$4.279x10^5$
MgB_2 + 10% TiO_2/SiO_2	750°C 1H	21	9	166	252.3	86.8	1.5	0.71	35.6	$3.381x10^5$

of the samples were conducted in a commercial Quantum Design Physical Properties Measurement System (PPMS). The samples were cut into a rectangular shape for measurements. Their dimensions were accurately measured by a digital micrometer. The typical dimensions of the samples used for magnetization measurement were 0.5mm x 2.5mm x 4.5 mm. H_{c2} and H_{irr} were defined as $H_{c2} = 0.9R(T_c)$ and $H_{irr} = 0.1R(T_c)$ from the resistance (R) versus temperature (T) curve. Details of the sample compositions, heat treatment conditions, and measured superconducting properties of all the un-doped and doped MgB2 samples are given in Table 1.

III. Results and Discussion

Fig. 1 contains the powder XRD patterns of MgB_2 samples with various doping ratios of TiO_2/SiO_2 at the sintering temperature of 750°C. MgO is the major impurity in all the samples. As the doping ratio increases from 0 wt% to 10 wt%, the amount of MgO obviously increases. The reason can be attributed to a reaction between the starting material Mg and the oxygen introduced by the dopant TiO_2/SiO_2 nanoparticles. Mg_2Si can be observed in the samples with TiO_2/SiO_2 doping. It is formed by the reaction of Mg and SiO_2. The amount of Mg_2Si seems to increase with increasing doping ratios. In addition, there are no peaks corresponding to TiO_2 (or Ti-containing compounds). However, energy dispersive x-ray spectroscopy (EDX) shows that the element Ti exists in the bulk samples. It is therefore suggested that the very weak XRD intensity of TiO_2 nanoparticles (as a second phase) is the main reason for the absence of TiO_2 peaks in the XRD patterns. Specifically, MgB_2 samples doped with TiO_2/SiO_2 nanoparticles had larger full width at half maximum (FWHM) values of the (110) peak than the pure sample, as described in Table 1. This indicates that small grains and various types of lattice defects or intra-granular precipitates [21] exist in the doped samples. This result might be related to lattice disorder due to oxygen doping into the MgB_2 lattice or Mg deficiency due to the existence of Mg_2Si. From Table 1, we can see that T_c for the TiO_2/SiO_2 doped samples was slightly depressed, due to impurity scattering. In addition, as the doping ratio increase, resulting in reduction of the superconducting volume of MgB_2, the self-field $J_c(0)$ dropped slightly at 20K.

Scanning electron microscope (SEM) images for the un-doped sample and the 10% TiO_2/SiO_2 doped one at two different magnifications are shown in Fig. 2(a)-(d). From the low magnification images (a) and (b), we can observe similar microstructures, consisting of fully round and smooth holes. Comparing Fig. 2(c) and (d) we can see that the un-doped sample shows noticeably better density and connectivity. The difference between the resistivities at 40K and 300K, $\Delta\rho$, values of MgB_2 bulks were 49.6 $\mu\Omega$ cm for the un-doped sample and 86.8 $\mu\Omega$ cm for the 10% doped sample, respectively. The low $\Delta\rho$ values are considered to originate from the good connectivity of the sample [22]. This is consistent with the higher low field J_c in the un-doped sample (Table 1). As Fig.2(c) and (d) shows, the grain size of the doped samples appears to be smaller than for the un-doped one, which is consistent with the broadening of the (110) X-ray peaks.

The resistivities, ρ, for the doped and un-doped samples sintered at 750°C are shown in Fig. 3. It can be observed that the resistivities for the doped sample are much higher than for the un-doped one. This trend is quite similar to that shown by SiC doped samples.

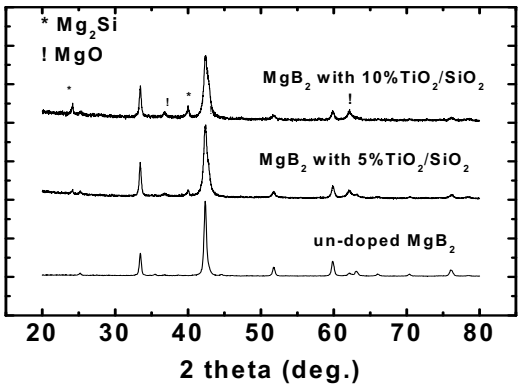

Figure 1 XRD pattern of MgB_2 samples with various doping rates at sintering temperature of 750°C.

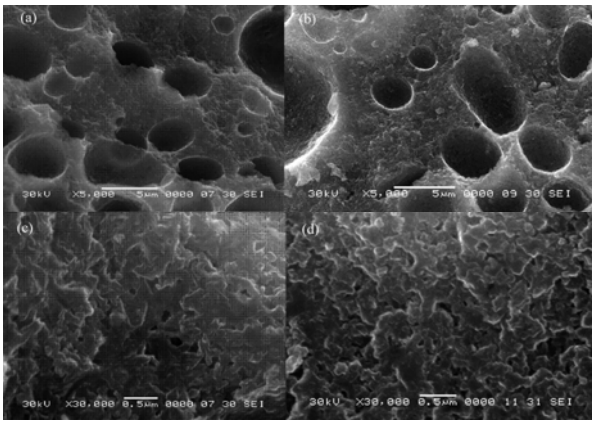

Figure 2 SEM images for un-doped (a), (c) and 10% TiO_2/SiO_2 doped (b), (d) MgB_2 samples sintered at 750°C for 1h.

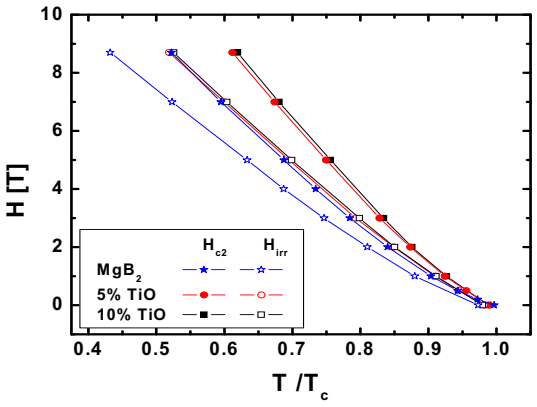

Figure 4 Temperature dependence of normalized H_{irr} and H_{c2} for un-doped and doped samples.

As ρ increases, H_{c2} and H_{irr} show an increasing trend as shown in Fig. 4. The straightforward explanation is that the doped samples are dirty, as the residual resistivity ratio (RRR), defined as R(300k)/R(40K), is found in Table 1 to also decrease with increasing doping level. Although Klie et al. [23] reported that most oxygen doping would result in second phases of MgO or BO_x with large particle size at the grain boundaries, several other reports [24], [25], [26] have revealed that there are nano $Mg(B,O)_2$ precipitates inside the MgB_2 grains, which have desirable effects on superconducting performance. Our current study on the effect of processing atmosphere on the superconducting properties of MgB_2 [20] have showed a high density of $Mg(B,O)_2$ precipitates and of grain boundaries as s result of oxygen doping. These desirable nanoprecipitates inside the MgB_2 grains result in lattice distortion and shorten the mean-free path (ℓ) of the superconducting electrons [25]. Therefore, the coherence length (ξ) is decreased due to the relation: $1/\xi = 1/\xi_0 + 1/l$, where ξ_0 is the value of ξ for the pure superconductor. According to $H_{c2} = \Phi_0/(2\pi\mu_0\xi^2)$, where Φ_0 is the

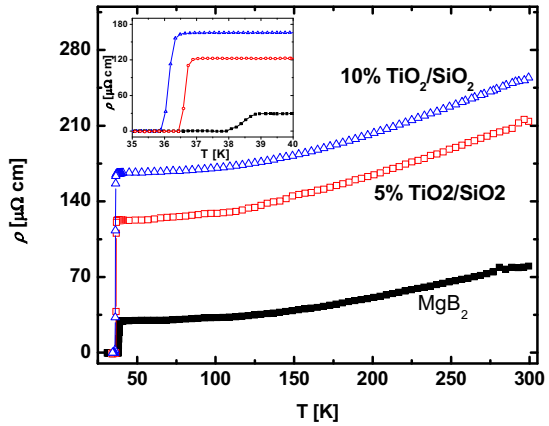

Figure 3 Resistivities versus temperature for un-doped and doped samples. An enlargement of the region around the critical temperature appears in the inset.

superconducting flux quantum and μ_0 is the magnetic permeability, H_{c2} will increase as ξ decreases. Both the H_{irr} and the H_{c2} slopes are found to be significantly higher for the doped samples. The best performance is shown in the 10% TiO_2/SiO_2 doped sample, which has a large FWHM of the (110) peak for the MgB_2 phase and a large ρ value at 40K, as shown in Table 1. This provides direct evidence that the lattice defects and precipitates are essentially beneficial for enhanced H_{irr} and H_{c2} for MgB_2 bulks.

IV. SUMMARY

In this paper, MgB_2 bulks doped with TiO_2 nanoparticles surface-modified by 5-10% SiO_2 were fabricated. The effects of the doping with TiO_2/SiO_2 nanoparticles on T_c, H_{c2} and H_{irr} have been investigated. It has been found that the additive TiO_2/SiO_2 nanoparticles resulted in small depressions in T_c, while H_{c2} and H_{irr} performances were improved due to the TiO_2/SiO_2 doping. The best performance was shown by the 10% TiO_2/SiO_2 doped sample. The enhancement of H_{c2} and H_{irr} can be attributed to the existence of precipitates induced by the TiO_2/SiO_2 doping.

ACKNOWLEDGMENT

The authors thank Dr. T. Silver and Dr. J. Horvat for their helpful discussions. This work was supported by the Australian Research Council, Australian Research Network for Advanced Materials, Hyper Tech Research Inc., and the University of Wollongong.

REFERENCES

[1] J. Nagamatsu, N. Nakagawa, T. Muramaka, Y. Zenitani, and J. Akimitsu, "Superconductivity at 39 K in magnesium diboride," Nature, vol. 410, pp. 63, Mar. 2001.

[2] D. C. Larbalestier, L. D. Cooley, M. O. Rikel, A. A. Polyanskii, J. Jiang, S. Patnaik et al., "Strongly linked current flow in polycrystalline forms of the superconductor MgB_2," Nature, vol. 410 pp. 186-189, March 2001.

[3] M. Kambara, N. H. Babu, E. S. Sadki, J. R. Cooper, H. Minami, D. A. Cardwell et al., "High intergranular critical currents in metallic MgB_2 superconductor," Supercond. Sci. Technol. vol.14, pp. L5-L7, April 2001.

[4] S. Souma, Y. Machida, T. Sato, T. Takahashi, H. Matsui, S.-C. Wang et al., "The origin of multiple superconducting gaps in MgB_2," Nature, vol. 423 pp. 65-67, May 2003.

[5] H. Kotegawa, K. Ishida, Y. Kitaoka, T. Muranaka, J. Akimitsu, "Evidence for Strong-Coupling *s*-Wave Superconductivity in MgB_2: ^{11}B NMR Study," Phys. Rev. Lett., vol. 87, pp. 127001-1-127001-4, August 2001.

[6] T. Takasaki, T. Ekino, T. Muranaka, H. Fujii, J. Akimitsu, "Multiple-gap structure of the binary superconductor MgB_2," Physica C, vol. 388–389, pp. 147-148, May 2003.

[7] J. S. Slusky, N. Rogado, K. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. M. Loureiro, M. K. Haas, H. W. Zandbergen, R. J. Cava, "Loss of superconductivity with the addition of Al to MgB_2 and a structural transition in $Mg_{1-x}Al_xB_2$," Nature, vol. 410, pp. 343-345, March 2001.

[8] S. X. Dou, S. Soltanian, J. Horvat, X. L. Wang, S. H. Zhou, M. Ionescu, H. K. Liu, P. Munroe and M. Tomsic, "Enhancement of the critical current density and flux pinning of MgB_2 superconductor by nanoparticle SiC doping," Appl. Phys. Lett, vol. 81, p. 3419, Oct. 2002.

[9] M. S. A. Hossain, J. H. Kim, X. L. Wang, X. Xu, G. Peleckis, S. X. Dou, "Enhancement of flux pinning in a MgB_2 superconductor doped with tartaric acid," Supercond. Sci. Technol., vol. 20 pp. 112-116, 2007.

[10] Y. Zhang, S. H. Zhou, A. V. Pan, S. X. Dou, " Effect of sucrose ($C_{12}H_{22}O_{11}$) doping on the critical current density of MgB_2," IEEE Trans. Appl. Supercond., vol. 17, No. 2, pp. 2933-2936, June 2007.

[11] C. H. Cheng, Y. Zhao, X. T. Zhu, J. Nowotny, C. C. Sorrell, T. Finlayson, H, Zhang, "Chemical doping effect on the crystal structure and superconductivity of MgB_2," Physica C, vol.386, pp. 588-592, 2003.

[12] M. Kühberger, G. Gritzner, "Effects of Sn, Co, and Fe on MgB_2," Physica C, vol. 370, pp. 39-43, 2002.

[13] S. X. Dou, S. Soltanian, W. K. Yeoh, and Y. Zhang, "Effect of nano-particle doping on the upper critical field and flux pinning in MgB_2," IEEE Trans. Appl. Suppercond., vol. 15, No. 2, pp. 3219-3222, June 2005.

[14] Y. Zhao, Y. Feng, D. X. Huang, T. Machi, C. H. Cheng, K. Nakao, N. Chikumoto, Y. Fudamoto, N. Koshizuka and M. Murakami, "Doping effect of Zr and Ti on the critical current density of MgB_2 bulk superconductors prepared under ambient pressure," Physica C, vol. 378-381, pp.122, October 2002.

[15] A. Yamamoto, J. Shimoyama, S. Ueda, Y. Katsura, S. Horii and K. Kishio, "Doping effects on critical current properties of MgB_2 bulks synthesized by modified powder-in-tube method," IEEE Trans. Appl. Supercond., vol. 15, pp. 3292-3295, 2005.

[16] J. Wang and Y. Bugoslavsky, A. Berenov, L. Cowey, A. D. Caplin, L. F. Cohen, L. D. Cooley, X. Song, D. C. Larbalestier, "High critical current density and improved irreversibility field in bulk MgB_2 made by a scaleable, nanoparticle addition route," Appl. Phys. Lett., vol. 81, pp. 2026-2028, September 2002.

[17] O. Perner, W. Häßer, J.Eckert, C. Fischer, C. Mickel, G. Fuchs, B. Holzapfel, L. Schultz, "Effects of oxide particle addition on superconductivity in nanocrystalline MgB_2 bulk samples," Physica C vol. 432, pp. 15-24, November 2005.

[18] A. Matsumoto, H. Kumakura, H. Kitaguchi, H. Hatakeyama, "Effect of SiO_2 and SiC doping on the powder-in-tube processed MgB_2 tapes," Supercond. Sci. Technol. Vol. 16, pp. 926-930, August 2003.

[19] G. J. Xu, J. C. Grivel, A. B. Abrahamsen, N. H. Andersen, "Enhancement of the irreversibility field in bulk MgB_2 by TiO_2 nanoparticle addition," Physica C, vol. 406, pp. 95-99, July 2004.

[20] S. X. Dou, Y. Zhang, X. Z. Liao, S. H. Zhou, G. Peleckis, A. V. Pan, X. L. Wang, "Effect of processing atmosphere on the microstructure and superconducting properties of MgB_2", unpublished.

[21] A. Serquis, Y. T. Zhu, E. J. Peterson, J. Y. Coulter, D. E. Peterson, and F. M. Mueller, "Effect of lattice strain and defects on the superconductivity of MgB_2," Appl. Phys. Lett., vol. 79, pp. 4399-4401, December 2001.

[22] J. M. Rowell, "The widely variable resistivity of MgB_2 samples," Supercond. Sci. Technol., vol. 16, pp. R17-R27, April 2003.

[23] R. F. Klie, J. C. Idrobo, N. D. Browning, K. A. Regan, N. S. Rogado, R. J. Cava, "Direct observation of nanometer-scale Mg- and Boxide phases at grain boundaries in MgB_2," Appl. Phys. Lett., vol. 79, pp. 1837–1839, Sep. 2001.

[24] X. Z. Liao, A. Serquis, Y. T. Zhu, J. Y. Huang, L. Civale, D.E. Peterson, and F. M. Mueller, H. F. Xu, "$Mg(B, O)_2$ precipitation in MgB_2," J. Appl. Phys., vol. 93, pp. 6208-6215, 2003.

[25] X. Z. Liao, A. C. Serquis, Y. T. Zhu, J. Y. Huang, D.E. Peterson, and F. M. Mueller, H. F. Xu, "Controlling flux pinning precipitates during MgB_2 synthesis," Appl. Phys. Lett. vol. 80, pp. 4398-4400, 2002.

[26] C. B. Eom, M. K. Lee, J. H. Choi, L. J. Belenky, X. Song, L. D. Cooley et al., "High critical current density and enhanced irreversibility field in superconducting MgB_2 thin films," Nature, vol. 411, pp. 558-560, May 2001.