Increased flux pinning force and critical current density in MgB$_2$ by nano-La$_2$O$_3$ doping

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Abstract. MgB$_2$ superconducting wires and bulks with nano-La$_2$O$_3$ addition have been studied. A series of MgB$_2$ superconducting bulk samples with nano-La$_2$O$_3$ addition levels of 0, 5, 7, 18wt% were prepared. AC resistivity data showed slight increases of $B_{c2}$ and unchanged $B_{so}$ for the bulk samples with doping levels lower than 7 wt% and decreased critical fields for the heavily doped (18 wt%) bulk. X-ray diffraction (XRD) showed the presence of LaB$_6$ in the nano-La$_2$O$_3$ doped MgB$_2$ bulk samples and decreased MgB$_2$ grain size in nano-La$_2$O$_3$ doped bulks. Monocore powder-in-tube (PIT) MgB$_2$ wires without and with 5 wt% nano-La$_2$O$_3$ addition (P-05) were prepared for transport property measurement. 2mol%C-doped Specialty Materials Inc. (SMI) boron powder was used for wire P-05 and previously prepared control wires (control wires were made without the addition of nano-La$_2$O$_3$ powder, W-00 and P2). Low field magnetic properties were obtained from magnetization loop (M−H), transport critical current density ($J_c$) was measured at 4.2 K for the nano-La$_2$O$_3$ doped PIT wire (P-05) and the control samples (P2 and W-00). The transport current critical density $J_c$ (B) of P-05 at 4.2 K and 8 T ($6.0 \times 10^4$ A/cm$^2$) was twice that of the control wire. The critical magnetic fields ($B_{c2}$ and $B_{so}$) of P-05 and the control sample P2 were compared. The critical fields of P-05 were slightly less than those of P2. Kramer-Dew-Hughes plots indicated a change from surface pinning to a mixture of volume pinning and surface pinning. It is shown that enhancement of P-05’s transport properties is due to additional flux pinning by the fine-size rare-earth borides rather than enhanced $B_{c2}$ or $B_{so}$.

1. Introduction
Since the discovery of MgB$_2$ superconductors in 2001 [1], substantial improvement on the material has been achieved in terms of critical field, transport property, wire manufacture processes. Due to the relatively high $T_c$ (39 K) in MgB$_2$ and the shortage of liquid helium worldwide, MgB$_2$ is particularly useful for helium-free MgB$_2$ MRI magnets [2] and is expected to replace Nb-based MRI magnets in the future. To reach these goals, improvements in the critical current density ($J_c$) of MgB$_2$ conductors are necessary.

Numerous approaches have been taken to produce MgB$_2$ materials with high transport properties: (1) chemical doping of MgB$_2$ wires [3-5]; (2) cold pressing [6-7]; (3) hot isostatic pressing (HIP) [8-9]; (4) the introduction of the internal magnesium diffusion (IMD) method to address porosity and connectivity issues [10-12]. So far, the best “non-barrier” transport $J_c$ values were obtained by the advanced internal
magnesium infiltration (AIMI) approach, with the addition of C and Dy₂O₃ (1.07 × 10⁶ A/cm²) at 10 T, 4.2 K, [13]. The AIMI technique has the benefit of forming dense MgB₂ layers with improved longitudinal connectivity compared to the extrinsic conventional powder-in-tube (PIT) method, which usually produces wires with randomly connected MgB₂ fibers. On the other hand, the PIT method is favored as a simple and inexpensive approach to studying wire properties in response to chemical doping.

Many chemicals have been added to MgB₂ in the past 18 years to study their effects on the resultant transport and other superconducting properties, such as upper critical field \(B_{c2}\) [14-15], and irreversibility field \(B_{irr}\) [16-17]. Generally, improvements in \(J_c\) have been attributed to the improvements of either \(B_{c2}\) or \(B_{irr}\). Till now, C has been shown to be the most effective doping element for the enhancement of \(B_{c2}\) [18] in MgB₂ materials. Many MgB₂ wires with high transport properties were doped with C or C-containing materials. In addition to C and C containing materials, doping with Dy₂O₃ has shown to increase both \(J_c\) and \(B_{irr}\) [19-20]. In particular, Chen et al. [19] and Li et al.[20] both demonstrated the effectiveness of a combination of flux pinning by Dy₂O₃ and carrier scattering by C. The effects on the transport \(J_c\) of rare earth oxide additions such as Pr₃O₁₁ [21-22], CeO₂ [23], Eu₂O₃ [24] have also been studied.

This paper describes the effect of adding nano-La₂O₃ dopants on superconducting and structural properties in MgB₂ superconductors. La₂O₃ was chosen because some rare-earth oxide additions have improved \(J_c\) and \(B_{c2}/B_{irr}\) [19-24] in MgB₂ superconductors. Besides, La₂O₃ doping has been previously studied for MgB₂ tapes and nano LaB₆ flux pinning centers as well as increase of \(J_c\) in the doped tapes were observed. Therefore, the effects of La₂O₃ doping in MgB₂ wires and bulks were studied here to fully explore the doping effect as well as the optimum doping level. Consequently, four different doping levels (0, 5, 7, 18 wt%) were chosen for the bulks and 5 wt% was chosen to make PIT wires based on the property measured for bulks with the same doping level. Transport \(J_c\) in the 5 wt% nano-La₂O₃ doped monocore PIT-processed MgB₂ wire increased to twice the value of the control sample at 4.2 K, 8 T.

2. Experimental

2.1. Sample preparation

2.1.1. Bulk samples. Four bulk samples B-00 (0 wt% La₂O₃ added), B-05 (5 wt% La₂O₃ added), B-07 (7 wt% La₂O₃ added) and B-18 (18 wt% La₂O₃ added) were made. The precursor powders used were 2 mol% C doped SMI boron powder, Mg powder (325 mesh) from Alfa Aesar, and nano-level (10-100 nm) La₂O₃ powder manufactured by US Research Nanomaterials Inc. The mole ratio of Mg to B powder used was 1:2. The powder was mixed inside a glove box, and then transferred to a hydraulic press for densification at 5000 psi (34.5 MPa). The resulting pellets were heat treated at 850 °C for 30 minutes in flowing Ar, followed by furnace cooling.

2.1.2. Wire Samples. The wire samples were prepared by Hyper Tech Research using their well-known “continuous tube filling and forming” (CFTT) powder-in-tube (PIT) process [25] followed by wire drawing to 0.83 mm in diameter. Selected for controls were two samples from previous studies. Designated P2 [26] and W-00 [27] precursor powders were 2 mol% C doped B from SMI and Mg powder as in the undoped bulk. The sample specifications are listed in Table 1.

| Sample Form | Sample Name | Wt% La₂O₃ | Heat Treatment | Crystallite size (nm) |
|-------------|-------------|-----------|----------------|-------------------|
| Bulk        | B-00        | 0         | 30min/850°C    | 20.6              |
| Bulk        | B-05        | 5         | 30min/850°C    | 19.8              |
| Bulk        | B-07        | 7         | 30min/850°C    | 7.6               |
| Bulk        | B-18        | 18        | 30min/850°C    | 17                |

Table 1. Info on bulk and PIT wire samples
Wire | P2* | 0 | 20min/675°C | -
---|---|---|---|---
Wire | W-00* | 0 | 60min/650°C | -
Wire | P-05 | 5 | 60min/650°C | -

*Previously made/published [26][27]
Both referred to as “Control”

2.2. Measurements

2.2.1. X-Ray diffraction (XRD) measurement. The powdered bulk samples were scanned on a Rigaku Miniflex 600 XRD machine at a scan rate of 5 deg / min. Phases and peaks were studied with the help of PDXL software.

2.2.2. AC resistivity. The AC resistivity vs temperature measurements on the bulk samples were performed on a Quantum Design Model 6000 Physical Property Measuring System (PPMS). The bulk samples were cut into rectangular prisms and four-point probe measurements were used to obtain sample resistance of 5 K to 45 K. The usual “10% normal resistivity” and “90% normal resistivity” rules were used to obtain \( B_{irr} \) and \( B_{c2} \), respectively.

2.2.3. Transport \( J_c \) measurement. The transport \( J_c \) measurements were carried out in transverse magnetic fields of up to 12 T in a liquid He bath at 4.2 K on samples 50 mm long with a gauge length of 5 mm and an electric field criterion of 1 \( \mu \)V/cm. Measurements were also done using a gauge length of 4 mm. The layer \( J_c \) of the CTFF PIT strands were calculated using the critical transport currents divided by the MgB\(_2\) layer area.

2.2.4. Magnetic \( J_c \) measurement. Magnetization-Magnetic field (M-H) loops were measured under VSM mode in a Quantum Design Model 6000 Physical Property Measuring System (PPMS) on sample P-05 3.2 mm long. Magnetic \( J_{cm} \) at 4.2 K was extracted from M-H loop at a ramp rate of 10 mT/s in transverse fields of up to 9 T. Based on Bean’s model [28], the 4.2 K magnetic \( J_{cm} \) for the superconducting CTFF monocore strand was calculated using:

\[
J_{cm} = \frac{3\pi\Delta M}{4d},
\]

where \( d \) is the diameter of the MgB\(_2\) layer inside the wire and \( \Delta M \) is the full height of the M-H loop at a certain field. The magnetic \( J_{cm} \) played a role in the pinning force calculation (see section 3.4).

3. Results and Discussion

3.1. Bulk sample’s magnetic and structure properties

\( B_{c2} \) and \( B_{irr} \) values were obtained for MgB\(_2\) bulks doped with nano-La\(_2\)O\(_3\) and the control bulk sample (B-00) at temperatures of 16 K ~ 36 K, Figure 1. \( B_{irr} \) stayed unchanged for B-05 and B-07. \( B_{c2} \) increased by 0.2 T with the addition of 5 wt% La\(_2\)O\(_3\) and increased by 0.4 T with addition of 7 wt% La\(_2\)O\(_3\). However, both \( B_{c2} \) and \( B_{irr} \) decreased significantly in response to doping with 18 wt% La\(_2\)O\(_3\). Based on the data in Figure 1, it can be seen that \( T_c \) of the doped bulks did not change compared to the control bulk sample. This is similar to the unchanged \( T_c \) observation on Dy\(_2\)O\(_3\) doped MgB\(_2\) bulks [29], meaning no significant atomic substitution occurred on MgB\(_2\) host lattice sites.
Phases and peaks in the MgB$_2$ bulk samples have been studied with the aid of XRD. The patterns shown in Figure 2 indicates the presence of LaB$_6$ in all doped bulk samples (shown by green arrows), presumably there are pinning centers. The MgB$_2$ peaks of B-05 and B-07, which is consistent with the minor increases of $Bc_2$ seen in Figure 1. The lattice shifts are smaller than those observed by Gao et al. [30] in MgB$_2$ tapes with acetone and La$_2$O$_3$ additions. Usually MgB$_2$ peak shifts observed in XRD patterns are caused by atomic substitution and/or strain. The shifts seen in Figure 3 is probably due to the lattice strain generated by the nanoparticles (such as LaB$_6$) since $T_c$ was shown to be unchanged in doped samples. MgB$_2$ grain size was estimated based on XRD data using William-Hall method, Table 1. As the La$_2$O$_3$ doping level increases from 0 wt% to 7 wt%, MgB$_2$ grain size decreased from 20.6 nm to 7.6 nm. The grain size of MgB$_2$ was 17 nm in the heavily doped sample. Yuan [27] observed same trend in his Dy$_2$O$_3$ doped MgB$_2$ bulks [27]. He attributed this grain size reduction to secondary phase DyB$_6$ nanoparticles. Here, the reduction of grain size in La$_2$O$_3$ doped MgB$_2$ bulks might be due to the secondary phase LaB$_6$, which inhibits the grain growth and pins fluxons.
Two common mechanisms for enhancing \( J_c \) in MgB2 wires are to enhance \( B_{irr} \) or enhance \( Bc_2 \). Here, we propose another mechanism for enhanced \( J_c \) in MgB2 wires with nano-La2O3 doping. It is well known that enhanced transport \( J_c \) by way of C doping in MgB2 wire can be attributed to enhanced \( Bc_2 \) by way of enhanced scattering effect [16, 19]. The increased transport \( J_c \) in Dy2O3-doped MgB2 wire was
attributed to an increase in $B_{irr}$ [19-20]. With regard to La$_2$O$_3$ doped wire samples, as mentioned above, the 4.2 K, 8 T, $J_c$ of P-05 was about twice that of the undoped control wire. But this increase is accompanied by no changes or decreases in $B_{C2}$ and $B_{irr}$ (1 T and 0.6 T, respectively, at lower temperatures), Figure 4. Clearly, a mechanism other than critical field is responsible for the increase in $J_c$; flux pinning is the obvious choice.

Figure 4. Upper critical field and irreversibility field for the control sample and nano-La$_2$O$_3$ added PIT MgB$_2$ wire P-05.

To further study the phenomena, Kramer plot has been made, A Kramer Plot, $J_c^{0.5}B^{0.25}$ vs. B, was shown in Figure 5. The irreversibility fields based on Kramer model [31], $B_k$, was taken at the x-axis intercepts of linear fittings (evenly spaced dashed lines) on Figure 5. $B_k$ of the doped wire has a lower value than the control wire value, which agrees with the critical field analysis done above on the wire samples.

Figure 5. Kramer plot ($J_c^{0.5}B^{0.25}$ vs. B) for control wire sample and P-05 at 4.2 K. The irreversibility fields based on the Kramer model [31], $B_k$, were taken as the extrapolated x-axis intercepts of linear fittings (evenly spaced dashed lines).
3.4. Flux pinning in response to La$_2$O$_3$ doping

Using data derived from the M-H loop, the normalized flux pinning force density $F_p/F_{p,max}$ was plotted against normalized magnetic field $b=B/B_k$ at 20 K to avoid flux jump effect, Figure 6(a). $B_k$ here was derived based on magnetic measurement conducted at 20 K in PPMS. Figure 6(b) showed the $J_c$ data measured by transport and magnetic methods. Apparently, magnetic measured $J_c$ agrees well with the transport data for P-05. Based on Dew-Hughes’s analysis [32] about $f_p \propto b^{1/2}(1 - b)^2$, the curve for the control sample which peaks at $B/B_k = 0.2$ is indicative of grain boundary pinning. In contrast, the curve for P-05 wire peaked at around $b = 0.168$. This phenomenon has been observed in Dy$_2$O$_3$ doped samples [29] and Yang et al. [29] stated that two reasons can be responsible for this behaviour: (1) The doped sample might contain a set of local $B_s$ instead of one distinct value, which can lead to an artificial error in the estimation of the peak positions; (2) The deviation from $b_{peak} = 0.2$ might be due to other pinning mechanisms (e.g., normal volume pinning in which $f_p$ maximizes at $b < 0.2$ due to anisotropy [33]) in association with the GB pinning. The presence of LaB$_6$ peaks in all the XRD patterns of the doped bulk samples strongly suggests that LaB$_6$, formed by reaction with the B powder, would also be present in the doped wires and as such would be responsible for the observed volume pinning.

Figure 6. (a, left) Normalized flux pinning force as a function of reduced field for control sample and the doped wire, P05, based on the magnetic data; (b, right) Critical current density measured for wire P-05 using both magnetic measurement and transport measurement.

4. Concluding Discussion

Four MgB$_2$ bulk samples with 0-18 wt% nano-La$_2$O$_3$ additions and a monocore PIT MgB$_2$ wire with 5 wt% nano-La$_2$O$_3$ addition were prepared for measurements of $J_c$, $B_{irr}$, $B_{c2}$ and magnetic and transport $J_c$ (see Table 1). Resistive measurements of $B_{irr}$ and $B_{c2}$ in response to La$_2$O$_3$ doping were made in the PPMS on the bulk and wire samples. For the bulks $B_{irr}$ remained unchanged in B-05 and B-07 but decreased in B-18; $B_{c2}$ increased by 0.2 T in B-05 and 0.4 T in B-07 but also decreased in B-18. For the wires (controls and P-05) $B_{irr}$ decreased by ~0.6 T at low temperatures and a smaller amount at high temperatures. $B_{c2}$ decreased by 1 T at low temperatures (resistive results and Kramer plot) and insignificantly at high temperatures. The 4.2 K, 8 T, $J_c$ of P-05 was about twice that of the undoped control. There is no correlation between changes in the critical fields and $J_c$. On the other hand, the occurrence of LaB$_6$ in the XRD patterns and the shapes of the normalized flux pinning curves (after Dew-Hughes) indicate that the increase in $J_c$ is a consequence of increased flux pinning in the doped wire.
5. References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Nature 410 63
[2] Zhang D, Kovacs C, Rochester J, Majoros M, Wan F, Sumption M D, Collings E W, Rindfleisch M, Panik D, D Doll D and Avonce R 2018 Supercond. Sci. Technol. 31 085013
[3] Matsumoto A, Kumakura H, Kitaguchi H and Hatakeyama H 2003 Supercond. Sci. Technol. 16 926
[4] Ma Y, Zhang X, Xu A, Li X, Xiao L, Nishijima G, Awaji S, Watanabe K, Jiao Y, Xiao L and Bai X 2005 Supercond. Sci. Technol. 19 133
[5] Woźniak M, Hopkins S C, Gajda D and Glowacki B A 2012 Phys. Procedia 36 1594-8
[6] Hossain M S, Senatore C, Flükiger R, Rindfleisch M A, Tomasic M J, Kim J H and Dou S X 2009 Supercond. Sci. Technol. 22 095004
[7] Wan F, Sumption M D, Rindfleisch M A and Collings E W 2017 IOP Conference Series: Materials Science and Engineering Vol. 279, No. 1, p. 012024
[8] Gajda D, Morawski A, Zaleski A, Cetner T, Malecka M, Presz A, Rindfleisch M, Tomasic M, Thong C J, Rindfleisch M A, Susner M A, Rindfleisch M A, Thong C J, Tomasic M J and Collings E W 2013 Supercond. Sci. Technol. 26 115002
[9] Prikhna T, Gawalek W, Savchuk Y, Soldatov A, Sokolovsky V, Eisterer M, Weber H W, Noudem S, Demaere J, Wilke R H, Chen K, Weng X, Redwine J, Bark C W and Voyles P M 2011 Supercond. Sci. Technol. 24 137-50
[10] Li G Z, Sumption M D, Zwyer J B, Susner M A, Rindfleisch M A, Thong C J, Tomasic M J and Collings E W 2013 Supercond. Sci. Technol. 26 095007
[11] Ye S J, Matsumoto A, Togano K and Kumakura H 2011 Physica C 471 1133-6
[12] Kováč P, Hušek I, Melišek T, Kopena L and Kulich M 2016 Supercond. Sci. Technol. 29 10LT01
[13] Li G Z, Sumption M D, Susner M A, Yang Y, Reddy K M, Rindfleisch M A, Tomasic M J, Thong C J and Collings E W 2012 Supercond. Sci. Technol. 25 115023
[14] Patnaik S, Gurevich A, Bu S D, Kaushik S D, Choi J, Eom C B, Labalestier D C 2004 Phys. Rev. B 70 064503
[15] Angst M, Bud’ko S, Wilke R H and Canfield P C 2005 Phys. Rev. B 71 144512
[16] Sumption M D, Bhatia M, Dou S X, Rindfleisch M, Tomasic M, Arda L, Ozdemir M, Hascicek Y and Collings E W 2004 Supercond. Sci. Technol. 17 1180
[17] Wang J, Bugoslavsky Y, Berenov A, Cowey L, Caplin A D, Cohen L F, MacManus Driscoll J L, Cooley L D, Song X and Labalestier D C 2002 Appl. Phys. Lett. 81 2026-8
[18] Dai W, Ferrando V, Pogrebnyakov A V, Wilke R H, Chen K, Weng X, Redwing J, Bark C W, Eom C B, Zhu Y and Voyles P M 2011 Supercond. Sci. Technol. 24 125014
[19] Chen S K, Wei M, MacManus-Driscoll J L 2006 Appl. Phys. Lett. 88 192512
[20] Li G Z, Sumption M D, Rindfleisch M A, Thong C J, Tomasic M J and Collings E W 2014 Appl. Phys. Lett. 105 112603
[21] Pan X F, Shen T M, Li G, Cheng C H and Zhao Y 2007 Phys. Status Solidi A 204 1555-60
[22] Ojha N, Malik VK, Bernhard C and Varma G D 2010 Phys. Status Solidi A 207 175-82
[23] Pan X F, Cheng C H and Zhao Y 2011 J Supercond. Nov Magn 24 1611-6
[24] Ojha N, Malik V K, Bernhard C and Varma G D 2009 Physica C 469 846-51
[25] Tomasic M, Rindfleisch M, Rue M, McFadden K, Doll D, Phillips J, Sumption M D, Bhatia M, Bohnenstiehl S and Collings E W 2007 Physica C 456 203-8
[26] Li G Z, Yang Y, Susner M A, Sumption M D, Collings E W 2011 Supercond. Sci. Technol. 25 025001
[27] Yang Y 2016 Influence of Chemical Doping on Microstructures and Superconducting Properties of MgB2 Wires and Bulk Samples (Doctoral dissertation, The Ohio State University)
[28] Sumption M D, Peng X, Lee E, Wu X and Collings E W 2004 Cryogenics 44 711
[29] Yang Y, Sumption M D and Collings E W 2016 Sci. Rep. 6 29306
[30] Gao Z, Wei Y M, Wang D, Z Xian-Ping, Satoshi A and Kazuo W 2010 Chin. Phys. Lett. 27 117401
[31] E. J. Kramer 1973 J. Appl. Phys. 44 1360
[32] Dew-Hughes D 1974 Phil. Mag. 30 293-305
[33] Eisterer M 2008 Phys. Rev. B. 77 144524