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Synergetic combination of LIMD with CHPD for the production of economical and high performance MgB2 Wires

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Abstract

We propose an economical fabrication concept, the localized internal magnesium diffusion (IMD) method. Instead of using a single magnesium (Mg) rod in the center of a metal sheath tube, we use large-sized Mg particles (20-50 mesh) mixed well with cheap 97% crystalline boron powder to fill the metal sheath tube. After a repeated drawing process, the coarse Mg is elongated along the core wire axis of the metal sheath tube. Textured MgB2 grains are then formed during the sintering process. In the localized IMD process, however, there is still a need to improve the overall density. In order to increase the density of the composite, a modified cold high pressure densification (CHPD) technique has been applied before the reaction. It is found that the critical current density (Jc) of the sample made from large-sized Mg with crystalline boron powder and treated by CHPD is increased significantly, so that it is quite comparable with the Jc values of samples made from expensive small magnesium and nanosized amorphous boron powder. At 4.2 K and 8 T, the Jc value of the wire in this work with the cheapest starting materials reaches 10 000 A/cm2 , which is similar to reported values for samples made by the powder-in-tube and IMD processes with expensive nanosized amorphous boron powder. A possible mechanism is proposed, and the microstructure is analyzed to explain this interesting feature. The main goal of this work is to develop a novel and cost-effective fabrication technique by combining the localized IMD process with CHPD and using cheap crystalline boron powder to manufacture MgB2 superconductor wires with electromagnetic performance superior to that of low-temperature Nb-Ti superconductors. 2002-2011 IEEE.

Keywords

mgb2, high, economical, performance, chpd, limd, production, synergetic, wires, combination

Disciplines

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Synergetic Combination of LIMD with CHPD for the Production of Economical and High Performance MgB_2 Wires

Minoru Maeda, Md. Shahriar Al Hossain, Ashkan Motaman, Jung Ho Kim, Anna Kario, Matt Rindfleisch, Mike Tomsic, Shi Xue Dou

***Abstract*— We propose an economical fabrication concept, the localized internal magnesium diffusion (LIMD) method. Instead of using a single magnesium (Mg) rod in the centre of a metal sheath tube, we use large-size Mg particles (20-50 mesh) mixed well with cheap 97% crystalline boron powder to fill the metal sheath tube. After a repeated drawing process, the coarse Mg is elongated along the core wire axis of the metal sheath tube. Textured MgB_2 grains are then formed during the sintering process. In the localized IMD process, however, there is still a need to improve the overall density. In order to increase the density of the composite, a modified cold high pressure densification (CHPD) technique has been applied before the reaction. It is found that the critical current density (J_c) of the sample made from large-size Mg with crystalline boron powder and treated by CHPD is increased significantly, so that it is quite comparable with the J_c values of samples made from expensive small magnesium and nanosize amorphous boron powder. At 4.2 K and 8 T, the J_c value of the wire in this work with the cheapest starting materials reaches 10,000 A/cm^2, which is similar to reported values for samples made by the powder-in-tube (PIT) and IMD processes with expensive nanosize amorphous boron powder. A possible mechanism is proposed, and the microstructure is analyzed to explain this interesting feature. The main goal of this work is to develop a novel and cost effective fabrication technique by combining the localized IMD process with CHPD and using cheap crystalline boron powder to manufacture MgB_2 superconductor wires with electromagnetic performance superior to that of low temperature Nb-Ti superconductors.**

***Index Terms*—Critical current density, crystalline boron, localized diffusion, elongated Mg.**

I. Introduction

So far as practical applications are concerned, the preparation methods play a very important role in achieving good performance. The '*in situ*' method has been used successfully to make MgB_2 wires and tapes. In most cases, both high purity crystalline or amorphous boron (B) powder and small size Mg are used to make the MgB_2 conductor [1-4]. If this wire is to be applied in an industrial application, however, the costs of the raw materials will be significantly increased and need to be taken into serious consideration. The material cost could be decreased significantly by using low-grade precursors. High purity (99%) amorphous B powder is about ten times more expensive than low purity (96%) crystalline powders. Alternative lower purity materials need to be tested to find out if they can be used to prepare MgB_2 without much deterioration in the superconducting properties. Recently, Kim et al. [5] proposed a very cost effective fabrication process that involved tailoring the starting material for high performance MgB_2 wire. It was reported that using carbon (C)-encapsulated crystalline boron powder and coarse Mg as precursors worked to improve the MgB_2 grain linkage by controlling the shape and direction of the voids; however, grain connectivity is still affected by the presence of elongated voids. To date, the low density within the filament cores has been a serious obstacle to reaching high critical current density (J_c) values in MgB_2 wires fabricated by the *in situ* processing technique. In addition, the reaction of Mg and B to form MgB_2 involves a volume contraction that produces a final density limited to about 50 % of the theoretical density (2.36 g/cm^3). The high porosity is well known to be difficult to avoid. As a result, the grain connectivity is hampered by the presence of voids in the finished wires. The typical effective superconductor area in the wire is only about 10% [6, 7]. Recently, cold high pressure densification (CHPD) has been suggested as an alternative to enhance mass density and probably grain linkage [8, 9]. The J_c at 4.2 K and 10 T has been reported to be increased to ~40,000 A·cm^{-2} for a malic acid doped square conductor produced using CHPD. The first successful CHPD of a dense MgB_2 conductor in a short-length (< 1 m) was reported by the University of Geneva in 2009 [8]. The density increased from 50% for normal wire to 73% for the CHPD wire after heat treatment. The J_c increase was particularly impressive at 20 K, amounting to more than 300%. Another very effective densification technique is called the infiltration method, first reported by Giunchi *et al.*, in which the MgB_2 wire was fabricated using a composite billet composed of a steel pipe internally lined with an Nb tube filled with a coaxial internal pure Mg rod and B powder [10]. The J_c performance from the

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reported work was not outstanding, however, as there was no chemical doping associated with the technique. Following this work, an internal Mg diffusion (IMD) process using a pure Mg rod as a core surrounded by B powder and SiC additive was developed. The composite was cold worked into a wire and heat-treated at temperatures above the melting point of Mg (650 °C). During the heat treatment, liquid Mg infiltrated into the B layer and reacted to form MgB_2 phase. The best J_c for this IMD SiC doped MgB_2 wire was 100,000 $A\cdot cm^{-2}$ at 8 T [11], exceeding the performance of commercial Nb-Ti wires and making it satisfactory for all technical applications. However, there is a serious limitation for scaling-up the IMD method. In this process, the Mg infiltration into the B layer forms a hollow wire with only a thin layer of MgB_2 in the interior of the sheath tube. The total superconductor cross-sectional area is small. It is obvious that for this technique to be useful in large-scale production, an innovative process must be developed, and this is the process we propose in this work.

The main goal of this work is to develop a novel fabrication technique by combining the localized IMD process (LIMD) with CHPD and using large size Mg instead of Mg rod and cheap crystalline B powder for the manufacture of economical MgB_2 superconductor wires with electromagnetic performance suitable for industrial application.

II. Experimental Procedure

All wires were fabricated by the *in situ* powder-in-tube (PIT) process. The starting Mg:B atomic ratio was chosen to be 1:2. Mg powders with different particle sizes of 325 mesh, 100 mesh, and 20-50 mesh were mixed with 97% crystalline boron supplied by Specialty Material Inc (SMI), USA. For comparison, two extra batches of wires were prepared from 325 mesh Mg/99% nanosize amorphous boron supplied by SB Boron USA and 325 mesh Mg/crystalline boron supplied by HC Starck, Germany. The compacted mixtures were inserted into Fe sheaths 9.5 mm in outer diameter and 5.5 mm in inner diameter. The Fe sheaths were cold-rolled into wires 3.5 mm in diameter using a two-axial grooved roller and inserted into Monel sheaths 6.0 mm in outer diameter and 3.5 mm in inner diameter. Afterwards, the composites were cold-rolled and drawn into wires 1.0 mm in diameter. The wires were then subjected to the CHPD process with the applied pressure of 1.5 GPa for core densification. All wires were sintered at 600 ^{o}C for 16 hours in a flowing argon gas environment. The transport critical currents of short pieces (6 cm) of straight wires were measured against magnetic field in the low temperature laboratories at the Karlsruhe Institute of Technology (KIT), Germany. Samples were immersed in a liquid helium bath and exposed to an external transverse magnetic field ranging from 2 up to 12 T. Current–voltage (I–V) characteristics were recorded by using a standard four-point measurement, where the potential taps were placed in the middle of the wire and spaced 2 cm from each other. The critical currents were estimated from the I–V curves using the criterion of 1 μV/cm. Grain morphology and microstructure were investigated by scanning electron microscopy (SEM).

III. Results and Discussions

Fig. 1 gives a comparison of J_c with and without CHPD in MgB_2 monofilament wires made from 325 mesh Mg and 99% purity amorphous (SB) or crystalline (SMI and Starck) B powders. The J_c of wires made from amorphous boron typically shows better performance compared to those from crystalline boron powders, which is in good agreement with published results in the literature [4]. The value of J_c was surprisingly enhanced, however, in MgB_2 wire made from crystalline boron by applying CHPD. The J_c of CHPD treated wire made from crystalline boron is 3 times higher than typical values measured for the same wires, but without applying CHPD. This value was similar to the J_c value of wire made from expensive high purity nanosize amorphous boron (SB). This result was the motivation for the selection of crystalline boron in this work. Crystalline boron mainly has the β-rhombohedral (β-rhB) structure, which is known to be quite stable, even at high temperature. This indicates that it is hard for it to fully react with Mg to form superconducting MgB_2 phase. After CHPD, however, elongated Mg might be diffused and connected well with the hard crystalline boron after sintering at 600 °C for 16 h, so that reaction paths are shorter and hence, the relative mass density in the filament is improved.

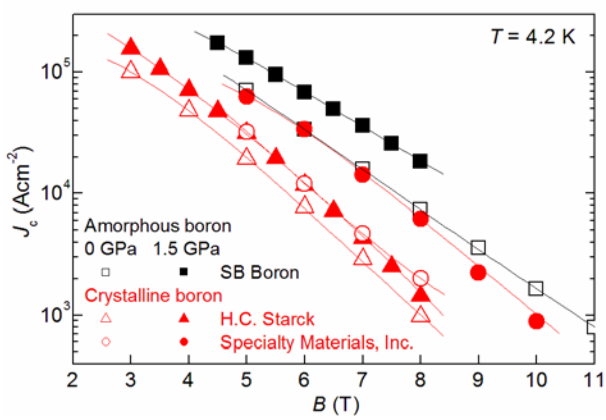

Fig. 1: Transport critical current densities at 4.2 K as a function of magnetic field for binary MgB_2/ Fe/ Monel wires fabricated from Mg powder with particle size of 325 mesh and various boron powders from SB Boron, H.C. Starck, and Specialty Materials, Inc. For comparison, the wires were also subjected to the CHPD process at 1.5 GPa.

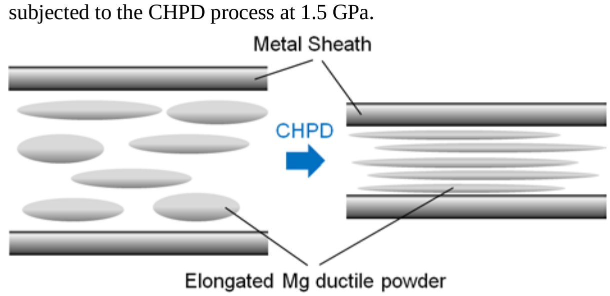

Fig. 2: Schematic concept of MgB_2 wire fabrication using combined effects of CHPD and localized internal Mg diffusion from large-size Mg particles.

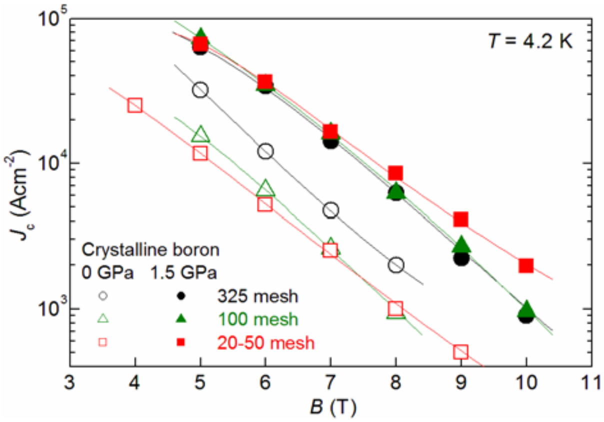

Fig. 3: Transport critical current densities at 4.2 K as a function of magnetic field for binary MgB_2/Fe/Monel wires fabricated from Mg powders with different particle sizes of 325, 100, and 20-50 mesh, and crystalline boron powder from Specialty Materials, Inc. For comparison, the wires were also subjected to the CHPD process at 1.5 GPa.

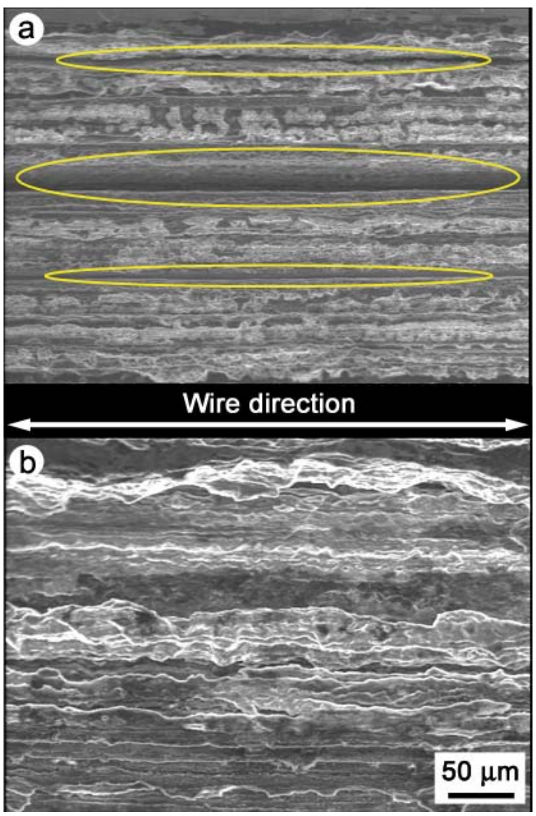

Fig. 4: SEM images of cores of sintered wires prepared from Mg powder with the large particle size of 20-50 mesh (a) before and (b) after CHPD. The areas marked by the yellow ellipses in (a) indicate elongated voids along the wire direction, and some of these are eliminated by CHPD.

In this study, we selected large size Mg following the concept proposed by Kim et al. [5], which was in contrast to the internal magnesium diffusion (IMD) method reported by the National Institute of Materials Science (NIMS) group [11]. We used large size Mg particles (100 mesh, 20-50 mesh) rather than using a single Mg rod in the centre of a metal sheath. By this technique, the Mg diffusion process was localized after long hours of heat treatment (600 °C/16 h) to allow a more uniform distribution of elongated voids generated during the cold working along the wire axis

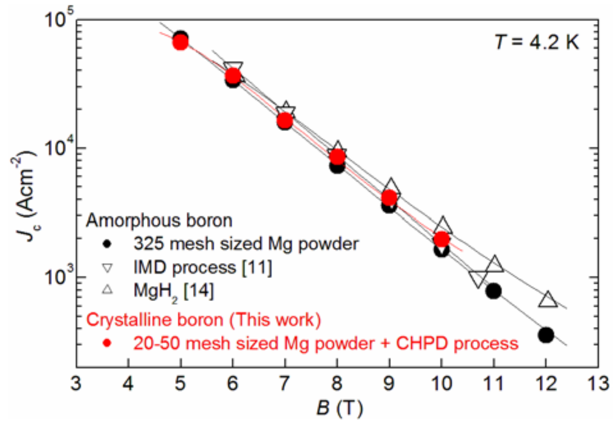

Fig. 5: J_c vs. B properties of binary wire using cheapest starting materials in this work compared with high performance reported wires using expensive nanosize amorphous powder.

rather than a single big hollow, as is found in the typical IMD wires after reaction. Kim et al. demonstrated the validity of this concept [5].

Although the localized IMD process only uniformly distributes the voids and changes the voids to an elongated shape, it slightly improves the overall density. Mg is ductile, and it can be stretched along the wire direction [12] during the drawing process, resulting in a stringy and fibrous structure, to which is attributed the improved superconducting area fraction. If the size, shape and distribution of the voids can be correctly identified, then it will be easier to find a solution to avoid it completely. CHPD is one of the most successful solutions for improving the density of the filament. Although voids can be minimized by CHPD, they are not completely avoided. The shape and direction may be controlled and more aligned, however, so that the MgB_2 grain linkage and area fraction can be improved. A schematic diagram of this mechanism is presented in Fig. 2.

Fig. 3 shows the effect of CHPD on the transport J_c at 4.2 K in magnetic fields up to 12 T for binary wires fabricated from various sizes of Mg powders and crystalline boron, and sintered at 650 °C/16 h. Only data above 3 T are shown, because in the lower field region, J_c was too high to be measured due to the limitations of the current supply source and the lack of proper electrical stabilization. It was found from Fig. 3 that the binary wire made from the smaller size (325 mesh) Mg powder usually showed higher values of J_c than the samples made from relatively larger sizes of Mg powder (100 and 20-50 mesh), which was consistent with literature data [13], but surprisingly, this behavior was changed completely when CHPD was applied. The J_c of wires fabricated from large size Mg (20-50 mesh) was significantly enhanced by applying CHPD due to the flat and elongated voids in the pressed region (Fig. 2), which might be attributed to the higher densification and hence, better connectivity in the filaments, as evidenced by the SEM images (Fig. 4). The aligned fibrous structure along the wire direction might also be the possible reason for the enhancement of the effective area fraction. Such grain alignment did not seem to be severely degraded inside the wire by applying CHPD (1.5 GPa), and the boundaries between filaments may also act as strong pinning centers. This work is still ongoing, and there is plenty of room for further investigations of this interesting feature of void engineering in the MgB_2 filaments after the reaction heat treatment.

The critical current density as a function of magnetic field was compared in this study with the reported best performance binary PIT *in situ* and IMD processed wires fabricated from expensive nanosize amorphous boron, small size Mg (325 mesh), MgH_2 [14], and Mg rod. It is clear from Fig. 5 that the wire fabricated in this work from the cheapest starting materials treated with CHPD was well comparable in terms of performance with reported binary wires fabricated from expensive precursors. The performance of the densified wire made from cheap crystalline boron and large-size Mg shows similar J_c-B properties to wires using expensive nanosize materials. The critical current density of the wire in this work reaches > 10^5 Acm^{-2} at 4.2 K and 4 T, which is within the feasible range for application in low-field magnetic resonance imaging (MRI) machines.

IV. Conclusion

We have shown the most economical fabrication route and an alternate solution to the IMD method for the development of high performance, cost-effective MgB_2 wires for industrial application. The J_c of CHPD treated wires made from crystalline boron and large-size Mg shows the best performance among the other wires in this study. The possible reason for increased J_c may be the flat, directional, and elongated voids that arise after heat treatment from large size ductile Mg during the cold working process. The core is densified by the application of CHPD without any severe deterioration of the filament inside the wire. The most noticeable point in this study is that such a good quality binary conductor using cheaper crystalline boron and large-size Mg can be equally useful and cost effective for industry, even without the use of nanoparticle dopants.

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References

[1] S. Zhou, A. V. Pan, J. Horbat, M. J. Qin, H. K. Liu, "Effects of Precursor Powders and Sintering Processes on the Superconducting properties of MgB_2", *Supercond. Sci*, Technol, vol. 17, 2004, S528.

[2] S. K Chen, K. A. Yates, M. G. Blamire, J. L. MacManus-Driscoll, "Strong Influence of boron precursor powder on the critical current density of MgB_2 ", *Supercond. Sci*, Technol, vol. 18, 2005, 1473.

[3] Y. Yang, M. A. Susner, M. D. Sumption, M. Rindfleisch, M. Tomsic, E. W. Collings, "Influence of Strand Design, Boron Type, and Carbon Doping Method on the Transport Properties of Powder-in-Tube $MgB_{2-x}C_x$ Strands ", *IEEE Trans. Appl. Supercon.*, vol. 22, 2012, 2.

[4] J. H. Kim, Y. U. Heo, A. Matsumoto, H. Kumakura, M. Rindfleisch, M. Tomsic, S. X. Dou, "Comparative Study of Mono- and Multi-Filament MgB_2 Wires with Different Boron Powders and Malic Acid Addition", *Supercond. Sci. Technol.* vol. 23, 2010, 075014.

[5] J. H. Kim, S. Oh, H. Kumakura, A. Matsumoto, Y. U. Heo, K. S. Song, Y. M. Kang, M. Maeda, M. Rindfleisch, M. Tomsic, S. Choi, S. X. Dou, "Tailored Materials for High-Performance MgB_2 Wire", *Adv. Mater.* vol. 23, 2011, 4942-4946

[6] J. M. Rowell, "The Widely Variable Resistivity of MgB_2 Samples", *Supercond. Sci. Technol.* vol. 16, 2003, R17.

[7] J. M. Rowell, "Critical Current Density and Resistivity in MgB_2 Films", *Appl. Phys Lett.* vol. 83, 2003, 102.

[8] R. Flukiger, M. S. A. Hossain, C. Senatore, "Strong Enhancement of J_c and B_{irr} in Binary *in situ* MgB_2 Wires After Cold High Pressure Densification", *Supercond. Sci. Technol.* vol.22, 2009, 085002.

[9] M. S. A Hossain, C. Senatore, R. Flukiger, M. A. Rindfleisch, M. J. Tomsic, J.H. Kim, S X Dou, "The enhanced J_c and B_{irr} of *in situ* MgB_2 Wires and Tapes Alloyed with $C_4H_6O_5$ (malic acid) After Cold High Pressure Densification", *Supercond. Sci. Technol.* vol. 22, 2009, 095004.

[10] G. Giunchi, S. Ceresara, G. Ripamonti, A. Di Zenobio, S. Rossi, S. Chiarelli, M. Spadoni, R. Wesche, P. L. Bruzzone, "High Performance New MgB_2 Superconducting Hollow Wires", *Supercond. Sci. Technol.* vol. 16, 2003, 285.

[11] J. M. Hurr, K. Togano, A. Matsumoto, H. Kumakura, H. Wada, K. Kimura, "Fabrication of High-Performance MgB_2 Wires by an Internal Mg Diffusion Process", *Supercond. Sci. Technol.* vol. 21, 2008, 32001.

[12] M. A. Susner, T. W. Daniels, M. D. Sumption, M. A. Rindfleisch, C. J. Thong, E. W. Collings, "Drawing Induced Texture and the Evolution of Superconductive Properties with Heat Treatment Time in Powder-in-Tube in situ Processed MgB_2 Strands", *Supercond. Sci. Technol.* vol. 25, 2012, 065002.

[13] D. L. Wang, Y. W. Ma, Z. G. Yu, Z. S Gao, X. P. Zhang, K. Watanabe, E. Mossang, "Strong Influence of Precursor Powder on the Critical Current Density of Fe-sheathed MgB_2 Tapes", *Supercond. Sci. Technol.* vol. 20, 2007, 574–578.

[14] H. Fujii, K. Togano, H. Kumakura, "Enhancement of Critical Current Densities of Powder-in-Tube Processed MgB_2 Tapes by Using MgH_2 as a Precursor Powder", *Supercond. Sci. Technol.* vol.15, 2002, 1571-1576.