In situ synthesis of superconducting MgB$_2$ fibers within a magnesium matrix

John D. DeFouw and David C. Dunand[a)]

Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

Composite wires, consisting of several hundred continuous MgB$_2$ fibers embedded within an Mg matrix, are produced by a casting method, whereby liquid Mg is pressure infiltrated into a preform of aligned B fibers which are subsequently reacted *in situ* to form MgB$_2$ fibers. Despite defects in the form of small, unreacted B islands and radial cracks from volume expansion, the MgB$_2$ fibers exhibit superconducting properties ($T_c = 39$ K and $J_c = 360$ kA/cm^2 at 5 K) comparable to the best results published for bulk MgB$_2$. The fibers are cylindrical and straight, allowing high packing densities within a mechanically tough, thermally dissipating, electrically conductive Mg matrix. The process is scalable to continuous lengths of superconducting Mg/MgB$_2$ wires. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1591243]

Since the discovery of superconductivity in MgB$_2$ at a critical temperature T_c of 39 K,[1] several processing methods have been developed to create MgB$_2$ wires and tapes with high transition temperatures and critical currents. The most studied approach has been the powder-in-tube (PIT) process, where powder is packed into a metal tube (~ 6–10 mm) which is then deformed to a 1–2 mm wire or tape.[2–10] The powder can be either MgB$_2$ (synthesized in a separate step) or a stoichiometric mixture of Mg and B powders. The wires are evaluated as deformed or after annealing, sintering, or reaction during a post-deformation heat treatment at temperatures between 200 and 1100 °C. The outer metal cladding provides strength and toughness (of importance given the brittle nature of MgB$_2$), as well as heat dissipation and normal conductivity in case of quenching. The MgB$_2$ wires fabricated by the PIT process are superconducting with T_c between 33 K (Ref. 9) and 39.6 K (Ref. 2) and have critical current densities J_c as high as 300 kA/cm^2 at 4.2 K and zero field,[2] with two cases[5,6] approaching 1 MA/cm^2 by extrapolating high-field J_c values to zero field at 4.2 K. Another method for producing thin MgB$_2$ wires is to react B fibers with Mg vapor at 950 °C.[11–15] The resulting free-standing MgB$_2$ fibers are superconducting at 39.4 K, exhibit much lower normal-state resistivity than bulk MgB$_2$, and have J_c values of ~ 400 kA/cm^2 at 5 K and zero field.[11] However, these reacted MgB$_2$ fibers are brittle and their shape is extensively deformed from the original straight, cylindrical shape of the B fibers.

In the present letter, we describe an *in situ* processing route which results in an Mg matrix composite containing straight, cylindrical, continuous MgB$_2$ fibers. The composite is created by infiltrating a preform of B fibers with liquid Mg and subsequently reacting these two phases at elevated temperatures. Superconducting properties of the resulting MgB$_2$ fibers are reported.

Boron fibers (from AVCO, with a diameter of 140 μm, a 15 μm tungsten core, and a nitrided surface) were cut to 25 mm length from a continuous spool. The fibers were bundled into an aligned preform which was placed in an iron crucible with 8 mm inside diameter. The ~ 670 fibers had a total mass of 0.652 g, corresponding to a preform volume fraction of 20.5%. Two 99.9% pure magnesium cylinders (from Alfa Aesar, Ward Hill, MA, with 4.411 g total mass) were placed on top of the preform of aligned fibers. The crucible was placed in a pressure infiltrator[16] where it was heated under vacuum to 800 °C and held for 30 min to ensure melting of the magnesium, which created a liquid seal above the fiber preform. The infiltrator was then pressurized with argon to 3.2 MPa in 2 min, forcing the liquid Mg into the evacuated space between the B fibers. After reducing the gas pressure to 0.1 MPa, the temperature was increased to ~ 950 °C and the composite was heat treated at that temperature for 2 h. The composite was then cooled to 650 °C in 23 min under a pressure of 1.4 MPa (to enhance cooling and feed shrinkage porosity) and subsequently cooled to 200 °C in 85 min. A control specimen was produced in a similar manner, except that cooling followed immediately after the infiltration step at 800 °C.

The samples were sectioned and polished following standard metallographic procedures.[16] The microstructure was observed with an optical microscope (using normal and cross-polarized light) and with a scanning electron microscope (Hitachi S-3500N) capable of energy dispersive x-ray spectroscopy (EDS). A 2 mm thick polished cross section of the heat treated composite was analyzed using time-of-flight secondary-ion mass spectrometry (SIMS) (Physical Electronics, PHI TRIFT III) with 25 keV energy and a 700 μm $\times 700 \mu$m raster size after *in situ* gallium-ion sputtering to clean the surface. X-ray diffraction (XRD) was performed using a Rigaku D/MAX-IA diffractometer ($\lambda = 0.154$ nm) on a portion of the heat-treated composite that had been ground into powder with mortar and pestle. Individual fibers were also extracted by dissolving the Mg matrix from a 9 mm long section of the reacted composite with a 10% HCl solution. Superconducting properties were determined on a single fiber, 6.4 mm long and 192 μm in diameter, using a superconducting magnetometer (Quantum Design MPMS5). The fiber

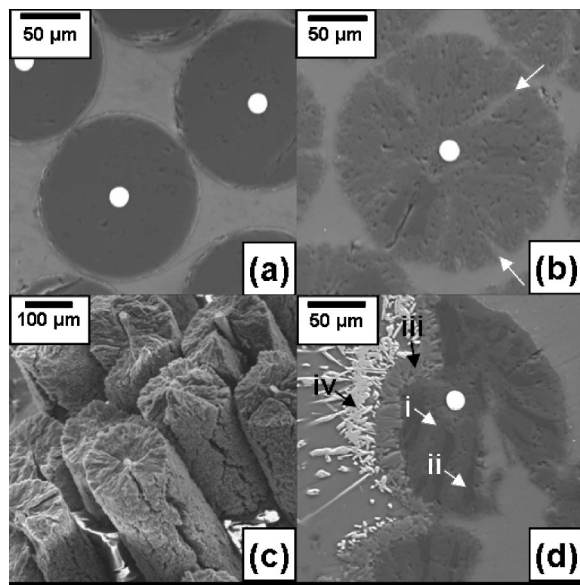a)Electronic mail: dunand@northwestern.edu

FIG. 1. Electron micrographs showing shape and morphology of infiltrated B fibers before and after heat treatment. (a) Unreacted composite showing 140 μm diameter B fibers in Mg matrix. (b) Reacted composite showing a 193 μm diameter MgB_2 fiber in Mg matrix, with radial cracks infiltrated with Mg. (c) Reacted composite showing parallel cylindrical MgB_2 fibers with radial cracks (HCl deep etch). (d) Reacted fiber near iron crucible wall with (i) MgB_2, (ii) unreacted B, and (iii and iv) two Fe–Mg–B phases with various amounts of Mg.

was mounted perpendicular to the applied field, cooled under -100 G and then warmed under zero field to determine T_c. Critical current densities were calculated inductively using the Bean model at 5 K and 20 K from M–H loops for the same fiber. Similar inductive measurements on single MgB_2 fibers were found to agree with transport J_c values.[11]

Observation by optical and electron microscopy of polished cross sections showed that the reacted composite was dense, with no significant porosity produced through the synthesis reaction or subsequent solidification. The control specimen cooled after infiltration without heat treatment showed no chemical reaction between the B fibers and the Mg matrix [Fig. 1(a)], as reported previously for similar Mg/B fiber composites.[17] Fast reaction to MgB_2 was however observed in a recent study[16] where B powders were infiltrated with liquid Mg at 800 °C, resulting in choking and preventing complete infiltration of the B preform. This difference in the reaction rate is most likely due to the much higher specific surface area of the discontinuous B powders (less than 44 μm in size),[16] as compared to the 140 μm continuous B fibers used presently.

After the 2 h heat treatment at 950 °C, several observations indicated that the B fibers had been converted to MgB_2. First, the fibers had grown to diameters of 196 ± 6 μm, [Fig. 1(b)], equivalent to the value of 190 ± 10 μm reported for MgB_2 fibers synthesized by reaction between free-standing 140 μm B fibers and Mg vapor.[13] This diameter compares well with a value of 191 μm calculated assuming that volume growth occurs in the radial direction only (with this assumption, the volume fraction MgB_2 fibers is calculated as 40.2% in the reacted composite). Second, the only boride in thermodynamic equilibrium with excess liquid or solid Mg is MgB_2.[16,18,19] Third, the cross section of reacted fibers exhibited birefringence when observed under
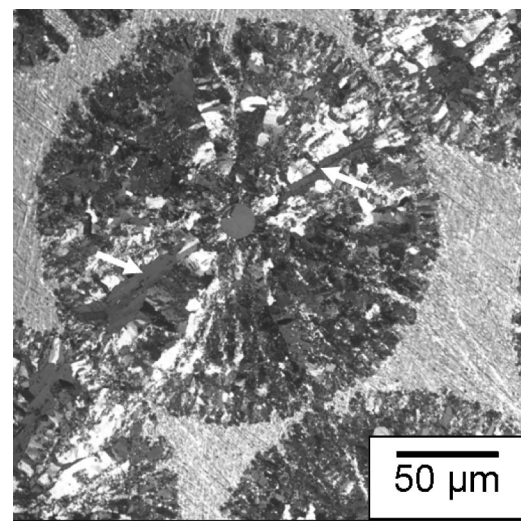
cross-polarized light (Fig. 2), a characteristic of bulk MgB_2. Fourth, the SIMS measurements showed the presence of both Mg and B within the fibers (Fig. 3). Direct proof of MgB_2 synthesis was provided by XRD analysis of composite powders, showing only Mg and MgB_2 peaks. Additionally, an extracted fiber was found to be superconducting at a critical temperature slightly above 39 K (Fig. 4), in good agreement with the value of 39 K for bulk MgB_2.[1] The critical current density of that fiber was calculated under zero-field conditions as 360 kA/cm^2 at 5 K and 210 kA/cm^2 at 20 K. Nearly the same values were found for free-standing MgB_2 fibers synthesized by reaction of B fibers with Mg vapor.[11] Optimization of this process through alloying or change of processing variables (e.g., heat-treatment temperature and time) to create pinning centers (e.g., grain boundaries and impurities) will probably lead to higher current densities,[14,20,21] which

FIG. 2. Optical micrograph of 200 μm MgB_2 fiber in Mg matrix under cross-polarized light. Arrows indicate slivers of non-birefringent material (unreacted B). A 15 μm W–B core is located at the center of the MgB_2 fiber. The interface between the matrix and fiber is well bonded.
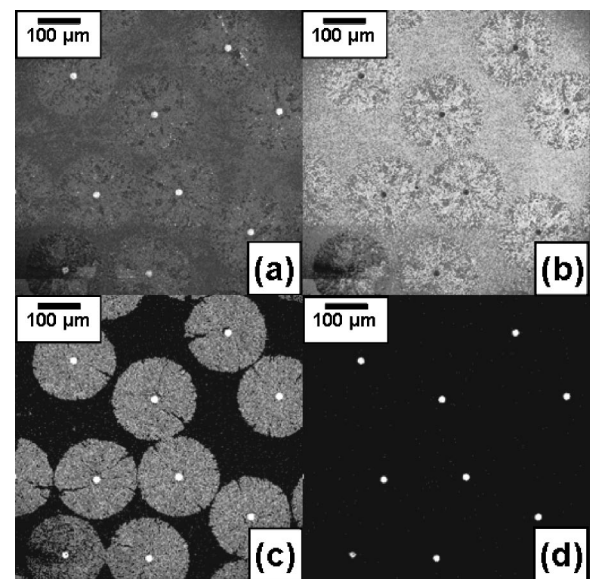

FIG. 3. SIMS elemental maps in reacted composite. (a) Total ion image. (b) Mg ion image, showing Mg in both matrix and fibers (except fiber cores). (c) B ion image, showing B exclusively within the fibers (and fiber cores). (d) W ion image, showing fiber cores.
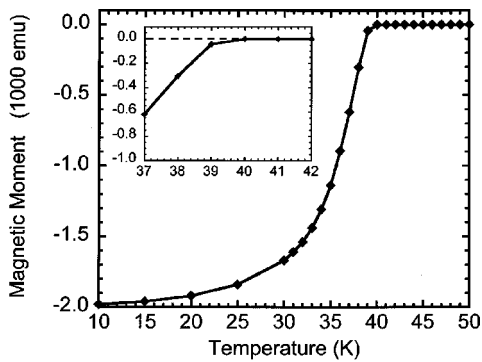
FIG. 4. Magnetic moment vs temperature under zero-field conditions for single MgB_2 fiber extracted from the reacted composite. Inset shows T_c slightly above 39 K.

will need to be confirmed by transport J_c measurements.

Unlike the irregular shape of the MgB_2 fibers produced by reaction in gaseous Mg,[11] the present MgB_2 fibers created by reaction with liquid Mg retained their original cylindrical shape [Fig. 1(c)]. Most of the fibers extracted by dissolution of the matrix had the same length as the composite specimen piece being dissolved (9 mm) and were straight. This was probably due to the much more uniform flux of Mg atoms provided by the Mg melt in direct contact with the B fibers, allowing a uniform diffusion front within the fibers, and thus a uniform volume expansion. However, this volume expansion ($\Delta V/V = 0.86$) was also probably responsible for the radial cracks observed for most fibers [Figs. 1(b), 1(c), and 2]. The cracks were filled with magnesium, which indicates that they formed during synthesis from the volumetric change, and not upon subsequent cooling from the mismatch in thermal expansion between Mg and MgB_2. Also, most MgB_2 fibers contained unreacted B in small, isolated radial slivers, which were visible under cross-polarized light (Fig. 2), but with a volume fraction too low to be measurable by XRD. These slivers were on average 10 μm wide and 40 μm long. Other unreacted areas were found in fibers nearest the iron crucible wall, which were only partially reacted to MgB_2, probably because a small amount of Fe dissolved into the Mg melt and reacted with the B fibers to form the Mg–Fe–B ternary phases [Fig. 1(d)] confirmed through EDS. This reaction could be avoided by using a different crucible (e.g., Ta or Ti) or by coating the Fe crucible with a stable ceramic such as MgO or Y_2O_3. Overall, the fiber/matrix interface appeared well bonded [Figs. 1(b) and 2], which is of importance for the mechanical properties of these composites. Based on these results, the present liquid-state process demonstrated here on a single small billet can easily be scaled up to the efficient and cost-effective production of continuous lengths of superconducting cables, since liquid metal infiltration is capable of creating several hundreds of meters of ceramic fiber/metal composites as demonstrated by Blucher et al.[22] for continuous Al_2O_3 fiber reinforced Al composites. By contrast, the creation of long lengths of composites with undamaged gas-phase synthesized MgB_2 fibers would be very challenging.

The synthesis of a composite, consisting of several hundred MgB_2 continuous fibers (with ∼40% volume fraction) aligned within a continuous Mg matrix, was achieved by infiltration of a B fiber preform with liquid Mg and subsequent *in situ* reaction at 950 °C. This processing route avoids the handling difficulties of brittle and deformed MgB_2 fibers synthesized in the vapor phase. It is adaptable to continuous infiltration techniques to produce continuous composite wires where a large number of fine MgB_2 fibers are embedded within a Mg matrix, which provides enhanced strength, toughness, and thermal and electrical conductivities. The MgB_2 fibers exhibit a critical temperature slightly above 39 K and a critical current density of 360 kA/cm^2 at 5 K and zero field, comparable with the best results of bulk MgB_2.

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).

[2] S. Jin, H. Mavoori, C. Bower, and R. B. van Dover, Nature (London) **411**, 563 (2001).

[3] G. Grasso, A. Malagoli, C. Ferdeghini, S. Roncallo, V. Braccini, A. S. Siri, and M. R. Cimberle, Appl. Phys. Lett. **79**, 230 (2001).

[4] H. Kumakura, A. Matsumoto, H. Fujii, and K. Togano, Appl. Phys. Lett. **79**, 2435 (2001).

[5] P. Kováč, I. Hušek, and T. Melišek, Supercond. Sci. Technol. **15**, 1340 (2002).

[6] H. Suo, C. Beneduce, M. Dhallé, N. Musolino, J. Genoud, and R. Flükiger, Appl. Phys. Lett. **79**, 3116 (2001).

[7] W. Goldacker, S. I. Schlachter, S. Zimmer, and H. Reiner, Supercond. Sci. Technol. **14**, 787 (2001).

[8] M. Eisterer, B. A. Glowacki, H. W. Weber, L. R. Greenwood, and M. Majoros, Supercond. Sci. Technol. **15**, 1088 (2002).

[9] K. Tachikawa, Y. Yamada, O. Suzuki, M. Enomoto, and M. Aodai, Physica C **382**, 108 (2002).

[10] S. Soltanian, X. L. Wang, J. Horvat, A. H. Li, H. K. Liu, and S. X. Dou, Physica C **382**, 187 (2002).

[11] P. C. Canfield, D. K. Finnemore, S. L. Bud'ko, J. E. Ostenson, G. Lapertot, C. E. Cunningham, and C. Petrovic, Phys. Rev. Lett. **86**, 2423 (2001).

[12] C. E. Cunningham, C. Petrovic, G. Lapertot, S. L. Bud'ko, F. Laabs, W. Straszheim, D. K. Finnemore, and P. C. Canfield, Physica C **353**, 5 (2001).

[13] R. A. Ribeiro, S. L. Bud'ko, C. Petrovic, and P. C. Canfield, Physica C **382**, 194 (2002).

[14] X. Song, S. E. Babcock, C. B. Eom, D. C. Larbalestier, K. A. Regan, R. J. Cava, S. L. Bud'Ko, P. C. Canfield, and D. K. Finnemore, Supercond. Sci. Technol. **15**, 511 (2002).

[15] Y. Wu, B. Messer, and P. Yang, Adv. Mater. (Weinheim, Ger.) **13**, 1487 (2001).

[16] D. C. Dunand, Appl. Phys. Lett. **79**, 4186 (2001).

[17] I. Ahmad and J. M. Barranco, Metall. Trans. **4**, 793 (1973).

[18] *Binary Alloy Phase Diagrams*, edited by T. Massalski (ASM International, Materials Park, OH, 1990).

[19] Z. Liu, D. G. Schlom, Q. Li, and X. X. Xi, Appl. Phys. Lett. **78**, 3678 (2001).

[20] Y. Zhao, Y. Feng, C. H. Cheng, L. Zhou, Y. Wu, T. Marchi, Y. Fudamoto, N. Koshizuka, and M. Murakami, Appl. Phys. Lett. **79**, 1154 (2001).

[21] Y. Zhao, Y. Feng, D. X. Huang, T. Machi, C. H. Cheng, K. Nakao, N. Chikumoto, Y. Fudamoto, N. Koshizuka, and M. Murakami, Physica C **378**, 122 (2002).

[22] J. T. Blucher, U. Narusawa, M. Katsumata, and A. Nemeth, Composites: Part A **32**, 1759 (2001).