In situ synthesis of superconducting MgB₂ fibers within a magnesium matrix

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(Received 21 March 2003; accepted 13 May 2003)

Composite wires, consisting of several hundred continuous MgB₂ 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 MgB₂ fibers. Despite defects in the form of small, unreacted B islands and radial cracks from volume expansion, the MgB₂ fibers exhibit superconducting properties \( T_c = 39 \text{ K} \) and \( J_c = 360 \text{ kA/cm}^2 \) at 5 K comparable to the best results published for bulk MgB₂. 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/MgB₂ wires. © 2003 American Institute of Physics. [DOI: 10.1063/1.1591243]

Since the discovery of superconductivity in MgB₂ at a critical temperature \( T_c = 39 \text{ K} \), several processing methods have been developed to create MgB₂ wires and tapes with high transition temperatures and current densities. The most studied approach has been the powder-in-tube (PIT) process, where powder is packed into a metal tube (\( \sim 6-10 \text{ mm} \)) which is then deformed to a 1-2 mm wire or tape. The powder can be either MgB₂ (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 MgB₂), as well as heat dissipation and normal conductivity in case of quenching. The MgB₂ 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/cm² at 4.2 K and zero field, with two cases\(^{5,6} \) approaching 1 MA/cm² by extrapolating high-field \( J_c \) values to zero field at 4.2 K. Another method for producing thin MgB₂ wires is to react B fibers with Mg vapor at 950 °C.\(^{11-15} \) The resulting free-standing MgB₂ fibers are superconducting at 39.4 K, exhibit much lower normal-state resistivity than bulk MgB₂, and have \( J_c \) values of \( \sim 400 \text{ kA/cm}^2 \) at 5 K and zero field.\(^ {11} \) However, these reacted MgB₂ 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 MgB₂ 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 MgB₂ 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 \( \sim 670 \) 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 \( \sim 950 \text{ °C} \) 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 x 700 µm 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 (\( \lambda = 0.154 \text{ nm} \)) 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

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was mounted perpendicular to the applied field, cooled under 
$-100 \text{ G}$ 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 $800 \degree C$, 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 $44 \mu m$ in size),$^{16}$ as compared to the 140 $\mu m$ continuous B fibers used presently.

After the 2 h heat treatment at 950 $\degree C$, several observations indicated that the B fibers had been converted to MgB$_2$. First, the fibers had grown to diameters of 196 $\pm 6 \mu m$, [Fig. 1(b)], equivalent to the value of 190 $\pm 10 \mu m$ reported for MgB$_2$ fibers synthesized by reaction between free-standing 140 $\mu m$ B fibers and Mg vapor.$^{13}$ This diameter compares well with a value of $191 \mu m$ 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 $360 \text{ kA/cm}^2$ at 5 K and $210 \text{ kA/cm}^2$ 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
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$_2$.

The authors acknowledge the help of D. B. Watkins in performing and evaluating the magnetometer experiments. This research was supported by a NSF grant (No. DMR-0233805), monitored by Dr. K. L. Murty.

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