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Composites consisting of Mg and MgB$_2$ phases were fabricated by liquid-metal infiltration following two routes. First, a preform of MgB$_2$ powders was pressure infiltrated at 800 °C with liquid Mg, which was subsequently solidified. Second, a preform of B powders was pressure infiltrated with liquid Mg at 700 °C, resulting in partial, *in situ* formation of the MgB$_2$ phase. Subsequent annealing at 950 °C increased the content of MgB$_2$ through reaction between B and Mg. All composites exhibited a pore-free structure with no significant additional phases and were superconducting near 39 K. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1427439]

The recently discovered MgB$_2$ superconductor[1] is difficult to use in bulk applications due to its brittleness. Cladding of MgB$_2$ wires or tapes with a ductile metallic sheath is one solution to this problem.[2–4] An alternative approach considered here is to create a metal matrix composite (MMC) consisting of a small-scale, isotropic mixture between the superconducting MgB$_2$ phase and a ductile metallic phase. The metal improves toughness and crack arrest, and also acts as a heat and electric conductor in case of localized breakdown in superconductivity in the MgB$_2$ phase. While the MMC approach is widely used for brittle ceramic cuprate and intermetallic niobium-based superconductors (with silver and copper matrices, respectively), we are aware of only two articles on MgB$_2$-based MMCs. In a first report,[5] Ti powders mechanically alloyed at room temperature with 4 wt % MgB$_2$ powders were found to react at 600 °C to form a ternary boride, which is probably nonsuperconducting. In a recent study,[6] a compacted mixture of MgB$_2$–11 wt % Al powders was vacuum sintered at 317 °C into a composite exhibiting superconductivity at 38 K; however, no information was given about its microstructure, e.g., porosity and reaction products between the phases.

A widely used method to fabricate MMCs is liquid-metal infiltration,[7] where a ceramic preform (consisting of packed powders, whiskers, or fibers) is infiltrated, usually under pressure to overcome capillary forces, by a metallic melt which is subsequently solidified. Among the candidate metals for infiltration of a MgB$_2$ preform, Mg stands out because of its low melting point and its inertness towards MgB$_2$.[8] In this letter, we demonstrate that superconducting MgB$_2$-based composites can be produced by pressure infiltration of liquid magnesium into preforms of magnesium diboride or boron.

In a first processing route, we used the standard pressure infiltration technique involving a MgB$_2$ preform and liquid Mg. A 14.1-mm-diam steel crucible was filled with 4.414 g of 99% pure MgB$_2$ powders (less than 44 μm in size, from Alpha Aesar). A quantity of 7.028 g of 99.99% pure Mg was placed above the tapped powder preform. The crucible was heated in an evacuated pressure infiltrator[9] to 800 °C in ~100 min and held at this temperature for 35 min. The infiltrator was then pressurized with argon to 3.5 MPa in ~1

min, thus pushing liquid Mg into the evacuated MgB$_2$ preform, and cooled to 200 °C in ~45 min. The resulting composite exhibits a density of 2.074 g/cm^3 as measured by water displacement, corresponding to a MgB$_2$ volume fraction of 38 vol % [using a density of 2.63 g/cm^3 for MgB$_2$ (Ref. 10)].

Optical and scanning electron microscope (SEM) observation of metallographic cross sections (polished with SiC paper in water and lapping with 1 μm diamond in oil) shows a fully infiltrated, pore-free composite (Fig. 1). The Mg matrix is found to neither react with, nor dissolve the MgB$_2$ particles. Figure 2 is an x-ray diffraction (XRD) spectrum (acquired with a Rigaku D/MAX-IA diffractometer with Cu $K\alpha$ radiation) showing that, beside the two main Mg and MgB$_2$ phases, the composite also contains small MgO amounts, probably formed by oxidation during processing. Further minor unidentified peaks cannot be matched to other magnesium boride phases. The small peak at 38° has been identified as the major B peak in a Mg–B reactivity study,[11] which may indicate that some elemental B is present, possibly from the as-received MgB$_2$ powders.

Four-point-probe conductivity measurements were conducted on a $15.5 \times 12.8 \times 1.4$ mm sample, with current leads press fitted at the end of the sample and voltage leads attached with silver epoxy, defining a measuring length of 5.0 mm. At ambient temperature, a resistivity of 16 $\mu\Omega$ cm was
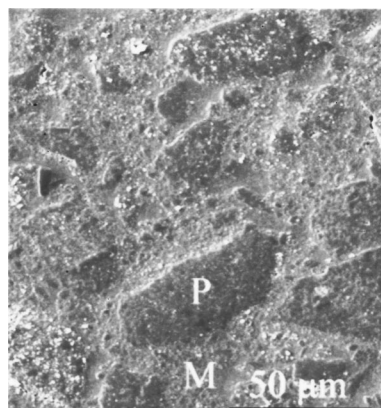

FIG. 1. SEM micrograph of the Mg/MgB$_2$ composite fabricated by pressure infiltration of MgB$_2$ powders with liquid Mg. The Mg matrix (M) is pore free and no reaction is visible at the MgB$_2$ particle (P) interface.

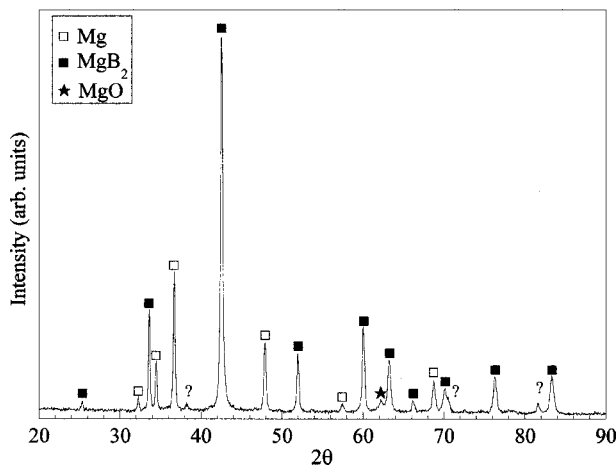[a)]Electronic mail: dunand@northwestern.edu

FIG. 2. XRD spectrum of Mg/MgB$_2$ composites fabricated by pressure infiltration of MgB$_2$ powders with liquid Mg.

FIG. 4. XRD spectra of composites fabricated by reactive pressure infiltration of B powders with liquid Mg (a) before annealing and (b) after annealing.

measured, as compared to 4.5 $\mu\Omega$ cm for pure Mg and ~16 $\mu\Omega$ cm for pure MgB$_2$.[12] The resistivity of the sample immersed in liquid He was zero up to an applied current of 12.0 A. The corresponding critical current density of 66 A/cm^2 is much lower than reported for sintered MgB$_2$,[12] due to the low connectivity of the superconducting MgB$_2$ phase in the MMC. Magnetic susceptibility was measured from 4 to 300 K in a magnetic field of 50 Oe after zero-field cooling, using a Quantum Design MPMS-5 magnetometer with a 6 cm sample travel. Figure 3 shows the onset of the magnetic transition at 38 K, close to the value of 39 K reported for pure, sintered MgB$_2$.[1] The transition width is, however, much larger than for pure MgB$_2$, as also reported for a sintered MgB$_2$/Al composite.[6] This was attributed to large areas having degraded local superconductivity (in our case, pure Mg, which is not superconducting) from the proximity effect and disorder.

As an alternate processing route, we investigated reactive pressure infiltration, where a preform of ceramic precursor is pressure infiltrated with a liquid matrix material which
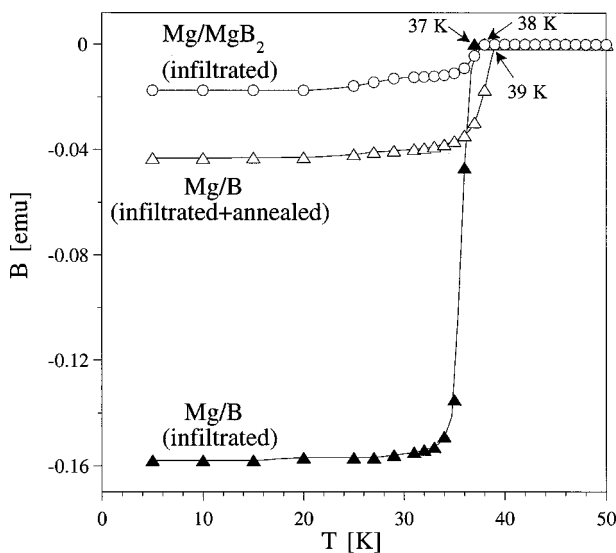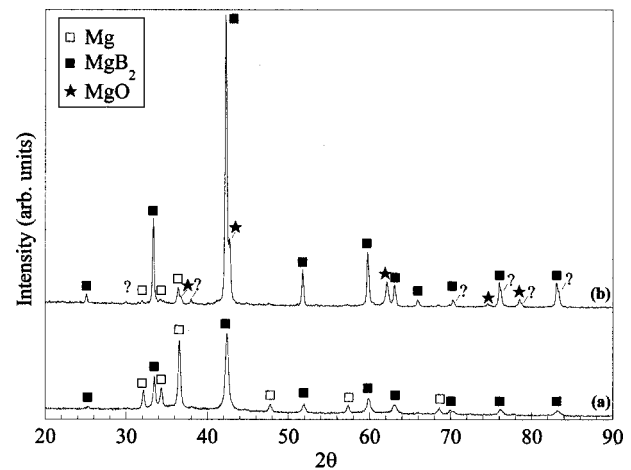

FIG. 3. Temperature dependence of magnetization of Mg/MgB$_2$ composites fabricated by pressure infiltration of MgB$_2$ powders with liquid Mg (Mg/MgB$_2$), and by reactive pressure infiltration of B powders with liquid Mg (Mg/B), before and after annealing.

reacts chemically to form the desired ceramic phase embedded in excess matrix material. This technique was applied, e.g., to synthesize SiC–Si composites by infiltrating a carbon preform with liquid silicon,[13] and it is used here to synthesize a Mg/MgB$_2$ composite by infiltrating and reacting a preform of boron powders with liquid magnesium. A quantity of 1.991 g of amorphous, 99.99% pure B powders (less than 44 μm in size, from Alpha Aesar) was lightly pressed into a steel crucible to a relative density of 30.8 vol %. The Mg metal, with a mass of 6.824 g, was separated from the preform by a nonwetting 2.4 mm layer of inert MgO powders (less than 149 μm in size, from Strem Chemical). The same infiltration procedure as above was used, except that the melt was held at 700 °C for 30 min. The core of the B preform was found to be uninfiltrated with Mg.

Optical microscopy of the infiltrated region revealed a gray, continuous, phase (with a few, small pores) and a few isolated metallic regions, consisting of veins (~50 μm in width and many millimeters in length) or islands (5–50 μm in size). The XRD spectrum [Fig. 4(a)] shows that these phases are MgB$_2$ and Mg, respectively, and that no other phases such as MgO or MgB$_4$, are present. Because they are amorphous, the original B powders are undetectable by XRD and optical micrographs showed no trace of them. However, SEM observation at higher magnification revealed that the gray majority phase contains micron-size inclusions, presumably B. While magnetic susceptibility measurements (Fig. 3) confirmed that the sample becomes superconducting, at 37 K, macroscopic samples with gauge length of ~6 mm exhibited nonzero resistivity at liquid-He temperature.

The above observations are consistent with partial reaction between B and Mg occurring during infiltration to form a discontinuous, superconducting MgB$_2$ phase within a compacted matrix of unreacted, amorphous boron, also containing large-scale inclusions of Mg. Such a structure could result from the compression of the loosely packed B preform by the pressurized melt, as reported for other infiltrated MMCs with deformable preforms.[14] Indeed, only a modest amount of preform compaction (i.e., from 30.8 to 38.4 vol % density) is sufficient to yield a MgB$_2$/B composite after complete reaction. The relatively low onset temperature of

37 K can be explained, as for the previous composite, by large areas of B and Mg with no local superconductivity.

A sample of reactively infiltrated composite was placed in an inert MgO bed, encapsulated in an evacuated quartz ampoule (together with some pure Mg to establish an atmosphere), and annealed at 950 °C for 30 min. This treatment was expected to lead to chemical equilibrium, based on a reports that Mg and B powders reacted completely to form MgB_2 upon holding for 2 h at 950 °C.[15] Indeed, Fig. 4 shows that the ratio of the main (100) MgB_2 peak to the main (101) Mg peak has increased from 1.2 before annealing to 18.5 after annealing, confirming synthesis of MgB_2 from Mg and B, and the almost complete disappearance of Mg. Also, small MgO peaks have appeared and may be due to reaction of Mg with residual O_2 or to incorporation of small amounts of MgO powders from the annealing bed. The critical current density could not be measured due to extreme sample brittleness. However, magnetic susceptibility measurements (Fig. 3) demonstrate that the sample becomes superconducting below 39 K, as reported for stoichiometric MgB_2 samples.[1]

In conclusion, we have demonstrated that superconducting Mg/MgB_2 composites could be fabricated by pressure infiltration of a MgB_2 preform with liquid Mg. Alternatively, pressure infiltration of a B powder preform with liquid Mg resulted in partial, *in situ* formation of the superconducting MgB_2 phase during the infiltration step, with further MgB_2 synthesis occurring upon subsequent heat treatment. This reactive processing approach is currently under investigation with B fiber preforms.

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