Superconductivity in Dense $MgB_2$ Wires

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$MgB_2$ becomes superconducting just below 40 K. Whereas porous polycrystalline samples of $MgB_2$ can be synthesized from boron powders, in this letter we demonstrate that dense wires of $MgB_2$ can be prepared by exposing boron filaments to $Mg$ vapor. The resulting wires have a diameter of 160 $\mu$m, are better than 80% dense and manifest the full $\chi = -1/4\pi$ shielding in the superconducting state. Temperature-dependent resistivity measurements indicate that $MgB_2$ is a highly conducting metal in the normal state with $\rho(40 \text{ K}) = 0.38 \mu\Omega\text{cm}$. Using this value, an electronic mean free path, $l \approx 600$ $\AA$ can be estimated, indicating that $MgB_2$ wires are well within the clean limit. $T_c$, $H_{c2}(T)$, and $J_c$ data indicate that $MgB_2$ manifests comparable or better superconducting properties in dense wire form than it manifests as a sintered pellet.

74.70.Ad, 74.25.Fy, 74.25.Ha, 74.60.Jg

I. INTRODUCTION

The discovery of superconductivity in $MgB_2$ has caused a renaissance of interest in intermetallic superconductivity. This, combined with the discovery of superconductivity in $YPd_2B_2C$ and the $RNi_2B_2C$ series several years ago, seems to indicate that the old idea of looking for high intermetallic $T_c$ values in compounds rich in light elements is still a valid guiding principle. Measurements of the boron isotope effect in this compound are consistent with the superconductivity being mediated via electron-phonon coupling, a conclusion that is also supported by recent bandstructural calculations. Measurements of the upper critical field, $H_{c2}(T)$, the thermodynamic critical field, $H_c(T)$, and the critical current, $J_c$, indicate that $MgB_2$ is a type-II superconductor with properties that are consistent with a intermetallic superconductor that has a $T_c \approx 40 \text{ K}$. For example, other than the remarkably high $T_c$, $MgB_2$ appears to be quite similar to $Nb_3Sn$. Given this similarity, and given the far lower density of $MgB_2$ as well as the greater natural abundances of $Mg$ and $B$, a logical question is whether wires of $MgB_2$ can be easily synthesized, and if so what are their physical properties. In this letter we present a remarkably simple method for the synthesis of $MgB_2$ wires from boron filaments. In addition, we show that wires produced in this manner are of high density and have impressively low normal state resistivity and impurity scattering.

II. EXPERIMENTAL METHODS

$MgB_2$ can be synthesized in powder form by reacting stoichiometric amounts of powdered $B$ and $Mg$ at 950°C for approximately an hour. Given that at 950°C the vapor pressure of $Mg$ is approximately 200 Torr, it is believed that $MgB_2$ forms via a process of diffusion of $Mg$ vapor into the boron grains. Based on this observation, the possibility of using this technique on other morphologies of boron appears to be promising.

$MgB_2$ wire was produced by sealing 100 $\mu$m diameter boron fiber, and $Mg$ into a Ta tube with a nominal ratio of $Mg_2B$. Given that $MgB_2$ is the most $Mg$ rich binary $Mg-B$ compound known, it was felt that excess $Mg$ would aid in the formation of the proper, stoichiometric phase. The sealed Ta tube was sealed in quartz and then placed into a 950°C box furnace for approximately an hour. The reaction ampoule was then removed from the furnace and quenched to room temperature.

Measurement of temperature and field dependent electrical resistivity and magnetization were performed in Quantum Design MPMS and PPMS systems. Resistivity measurements were made in a standard four probe geometry using Epotek H20E silver epoxy to make contacts. The contact resistance was approximately 1 Ohm. Given the well defined geometry of the samples, accurate measurements of resistivity were possible.

III. RESULTS

Upon opening the Ta tube it became clear that there had been a reaction between the boron fiber and the $Mg$ vapor. Whereas the boron fibers were straight and moderately flexible before the reaction, the $MgB_2$ wires in the Ta tube after the reaction were brittle and deformed. The inset of Figure 1 is a photograph of the resulting wires. As can be seen, there has been significant warping and bending of the fiber as a result of the reaction with the $Mg$ vapor. Figure 2 shows scanning electron microscope images of the fiber before the reaction as well

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as the wire after the reaction. In both cases a tungsten core (approximately 15 μm diameter) can be clearly seen. This core is part of the original boron fiber and does not appear to be effected by the exposure of the fiber to Mg, nor, as will be seen, does it seem to effect the superconducting properties of the resulting MgB₂ wire. Whereas the boron fiber has a diameter of 100 μm and breaks with a smooth, clean surface (inset to Fig. 1), the MgB₂ wire has a diameter of approximately 160 μm and breaks with a rougher, grainier surface. The increased diameter of the wire is consistent with observations that there is an expansion associated with the formation of the MgB₂ powders during synthesis. Although the MgB₂ wires were somewhat brittle, the integrity of the filament segments was preserved during the exposure to the Mg vapor, i.e. the fibers did not decompose or turn into powder.

Using a diameter of 160 μm and measuring the length and mass of several wire segments we determined the density of the wire to be 2.4 g/cm³. This is to be compared with a theoretical value of 2.55 g/cm³ for a single crystal sample using lattice parameters a = 3.14 Å and c = 3.52 Å for the hexagonal unit cell. Given the rather coarse nature of our measurements, this implies that the wire samples are probably better than 80% of the theoretical density. It should be noted that the small tungsten core would come in as a roughly 10% correction, and therefore is within our level of uncertainty.

Figure 1 presents the temperature-dependent magnetization of MgB₂. The data were taken after cooling in zero field and then warming in a field of 25 Oe. Given the aspect ratio of the wire segments used we were able to obtain a susceptibility very close to −1/4π, the value expected for total shielding and a demagnetization factor close to zero. Tc = 39.4 K can be determined from these data by using an onset criterion (2% of −1/4π). The width of the transition (10% - 90%) is 0.9 K.

Figure 3 presents the temperature-dependent electrical resistivity of MgB₂ wires. The room temperature resistivity has a value of 9.6 μOhm-cm whereas ρ(77 K) = 0.6 μOhm-cm and ρ(40 K) = 0.38 μOhm-cm. This leads to a residual resistivity ratio of RRR = 25.3. It should be noted that the shape of the resistivity curve and the RRR values are qualitatively the same as those observed for sintered pellets of polycrystalline Mg₁₀B₂. The relatively low room temperature resistivity value, along with high RRR are not unusual for diboride samples. The resistivity of the sintered pellet samples is approximately 1 μOhm-cm at 40 K. This somewhat higher value of the calculated resistivity for the pellet is consistent with the sintered sample having an actual density substantially lower than the theoretical value.

The temperature-dependent resistivity shown in Fig. 3 can be fit by ρ = ρ₀ + ρ₁T^α with α ≈ 2.6 between Tc and 200 K. This is comparable to the power law R = R₁ + R₂T^α with α₁ ≈ 2.8 found for the sintered Mg₁₀B₂ sample over a comparable temperature range. Given the similarity of the two power laws it seems clear that the resistivity of MgB₂ will not have a linear slope for temperatures between Tc and 300 K. On the other hand, using an average Fermi velocity v_F = 4.8 · 10^7 cm/s and a carrier density of 6.7 · 10²² cm⁻³ (two free electrons per unit cell) we can estimate the electronic mean free path to be approximately 600 Å at Tc. This is clearly an approximate value of the electronic mean free path, but given the estimated superconducting coherence length of approximately 50 Å these values place MgB₂ wires well within the clean limit. Given a κ ≈ 26, this implies that, much like the case of the RN₁₂B₂C materials, there may be significant non-local effects associated with MgB₂.

The superconducting transition temperature, Tc = 39.4 K, can be determined from both the magnetization and resistivity data shown in Figs. 1 and 3. This value is slightly higher than the Tc = 39.2 K value determined for isotopically pure Mg₁₁B₂, but is significantly lower that Tc = 40.2 K for Mg₁₀B₂. This is consistent with an approximate 80% natural abundance of ¹¹B. It is noteworthy that the superconducting transition is both relatively high and sharp in the wire samples. This means that either very few impurities are being incorporated into the MgB₂ or that what few impurities are being incorporated are having very little effect on either resistivity or Tc.

The temperature dependence of the upper critical field, H₂(T), is shown in the inset to Fig. 3. For each field three data points are shown: onset temperature, temperature for maximum dρ/dT, and completion temperature. Qualitatively these data are remarkably similar to the H₂(T) data inferred from measurements on Mg₁₀B₂ sintered pellets as well as recent measurements on hot-pressed powders. Quantitatively, at H = 9 T, the width of the resistive transition for the wire sample is roughly half of the width found for the sintered sample. These data are consistent with the wire sample being of comparable or better quality as the sintered powder samples.

Figure 4 presents data on the critical current Jc. The open symbols are Jc values extracted from direct measurements of the current dependent voltage across the sample at given temperature and applied field values. The filled symbols are Jc values inferred from magnetization loops by application of the Bean model. The direct measurement of Jc was limited to values below approximately 200 A/cm² due to resistive heating from the sample leads and contact resistance. As can be seen, the extrapolations of the directly measured, low Jc, data and the Bean-model-inferred, high Jc, data match up moderately well. In comparison to the Jc data presented for a sintered pellet of Mg₁₀B₂, Jc for the wire sample is roughly a factor of two higher at low fields and temperatures and over an order of magnitude higher at high fields.
IV. CONCLUSIONS

We have devised a simple technique of producing low resistivity, high density, high $T_c$ MgB$_2$ in wire form via exposure of boron filaments to Mg vapor. The resulting wire has better than 80% the theoretical density of MgB$_2$ and measurements of the temperature dependent resistivity reveal that MgB$_2$ is highly conducting in the normal state. The room temperature resistivity has a value of 9.6 $\mu$Ohm-cm whereas the resistivity at $T = 40$ K is 0.38 $\mu$Ohm-cm. This means that even in the normal state wires of MgB$_2$ can carry significant current densities. This should be compared with the resistivity of Nb$_3$Sn $\rho(20 \, K) = 11 \, \mu\text{Ohm-cm}$ and $\rho(300 \, K) = 80 \, \mu\text{Ohm-cm}$.

Given the well-defined geometry of the wire samples we have been able to directly measure a full $-1/4\pi$ susceptibility in the superconducting state. The values of $T_c$ for this wire sample are slightly higher than the $T_c$ values for isotopically pure Mg$_3$B$_2$ sintered powders and the width of the resistive superconducting transition is smaller than that seen for Mg$_3$B$_2$ sintered powders. In addition, $H_{c2}(T)$ for the wire sample is virtually the same as that found for Mg$_3$B$_2$ sintered pellets. Based on all of these observations it appears that MgB$_2$ wires provide dense, high quality samples of MgB$_2$. By comparing our estimate of the electronic mean free path $l \approx 600 \, \text{Å}$ to the superconducting coherence length $\xi \approx 50 \, \text{Å}$ we can see that MgB$_2$ wires are well within the clean limit.

All of the above, of course, presents the possibilities of using such wires for both research and applied purposes. For basic research the possibilities of making weak link Josephson junctions, SLUGS, and other devices are currently being pursued. On the applied side, given that boron filaments are produced in a variety of sizes and of arbitrary lengths, the possibility of converting boron filament into MgB$_2$ wire as part of a continuous process leads to the possibility of simple manufacturing of light weight, high $T_c$ wires with remarkably small normal state resistivities. In addition, this process could be used to turn boron coatings on tapes, cavities, or other devices into high-quality superconducting films. Although the low temperature $J_c$ values are currently smaller than those for Nb$_3$Sn, as of yet very little effort has been put into optimizing $J_c$. A multi-dimensional phase space of filament purity, diameter, treatment time and temperature has yet to be explored. Both basic and applied directions of research will have to be explored in detail over the coming months and years.

V. ACKNOWLEDGMENTS

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FIG. 1. Magnetization divided by applied field (25 Oe) for zero field cooled wire sample. Field was applied parallel to the wire length, leading to a demagnetization factor close to zero. Inset: photograph of wires as they appear after removal from Ta tube and part of U. S. dime for scale.

FIG. 2. Electron microscope image of cross section of grown MgB$_2$ wire. The diameter of the wire is 160 µm. Inset: electron microscope image of the un-reacted boron filament. The diameter of the filament is 100 µm. For both images the wire / filament was snapped in-situ. Note: In both images a central core of tungsten wire (diameter ≈ 15 µm) can be clearly seen.

FIG. 3. Temperature dependent electrical resistivity of MgB$_2$ wire. Lower inset: Expanded view for temperatures near $T_c$. Upper inset: $H_{c2}(T)$ data inferred from temperature dependent resistivity data taken in constant applied field upon cooling. The three symbols are for onset, maximum slope and completion temperatures.

FIG. 4. Superconducting critical current density, $J_c$, as a function of applied field every 5 K in 5 - 35 K range. Open symbols were taken via direct measurement of current dependent voltage of the wire. Filled symbols were determined via a Bean model analysis of magnetization data from wire samples with the applied field parallel to the wire length. The dashed lines simply connect data sets taken at the same temperature.