Synthesis and Processing of $MgB_2$ powders and wires

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Abstract

Sintered powders and wires of superconducting $MgB_2$ have been fabricated under a variety of conditions in order to determine details of the diffusion of the $Mg$ into $B$ and to study the types of defects that arise during growth. For samples prepared by exposure of boron to $Mg$ vapor at 950°C, the conversion of particles of less than 100 $\mu m$ size particles to $MgB_2$ is complete in about 2$h$. The lattice parameters of the $MgB_2$ phase determined from X-ray are independent of the starting stoichiometry and the time of reaction. Wire segments of $MgB_2$ with very little porosity have been produced by reacting 141 $\mu m$ diameter boron fibers in an atmosphere of excess $Mg$ vapor at 950°C. Defects in the reacted fibers are predominantly the voids left as the boron is converted to $MgB_2$. 

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I. INTRODUCTION

The discovery of superconductivity in the intermetallic compound, \( MgB_2 \) near 40 K\(^1\), has prompted both fundamental studies of the mechanism causing superconductivity and practical studies of supercurrent transport at grain boundaries. Bud’ko and co-workers\(^2\) have shown the existence of a boron isotope effect in that \( T_c \sim M^\alpha \) with \( \alpha = 0.26 \), where \( T_c \) is the superconducting transition temperature and \( M \) is the isotopic mass. This result implies that the electron-phonon interaction is important in the determination of \( T_c \) and that light elements with high phonon frequencies might be important in the search for new metallic superconductors with high transition temperatures. Energy gap measurements\(^5\) and neutron scattering measurements of the phonon spectrum\(^6\) all point to a conventional mechanism for the superconductivity. On the practical side, Canfield and co-workers\(^7\) have shown a method to convert commercially available boron fibers\(^8\) into very low resistivity \( MgB_2 \) wire and Takano and co-workers\(^9\) have measured the current carrying capacity of hot-pressed pellets of the material. Other measurements of flux pinning and intergrain coupling have been made using studies of flux creep\(^10\).

In this paper, we report a systematic study of the vapor diffusion method of sample preparation for both microcrystalline powders and boron (\( B \)) fibers, which are available commercially in kilometer lengths. The primary variable in the study is time, and for the wire samples the effect of defects in the starting \( B \) fibers. Of particular interest is the role of the tungsten-boride core in creating cracks and transmitting \( Mg \) along the length of the fiber.

II. EXPERIMENT

For powder synthesis, we place a stoichiometric mixture of bright lumps of \( Mg \) (99.9%) and fine crystalline \(^{11}\)\( B \) powder (99.5%) that is less than 100 \( \mu m \) in diameter into a \( Ta \) tube whose ends are sealed under a partial atmosphere of \( Ar \). For the wire synthesis, we cut \( B \) fiber lengths several \( cm \) long and either 100 \( \mu m \) or 141 \( \mu m \) in diameter and place them in \( Ta \) tubes under a partial pressure of \( Ar \) with excess \( Mg \). These starting \( B \) fibers have a tungsten-boride core about 15 \( \mu m \) in diameter with breaks every few \( cm \).

After the \( Ta \) tubes are sealed, they are in turn sealed in quartz ampoules with \( \sim 175 \) \( mbar \) of \( Ar \) and placed in a box furnace preheated to 950\(^\circ\)C. It is believed that using a preheated furnace inhibits the growth of higher boron phases. After reaction, the samples are rapidly cooled by putting the quartz tube in running cold water. The formation of \( MgB_2 \) from \( B \) causes the powders to expand and bow the \( Ta \) tube outward\(^2\) and causes 100 \( \mu m \) diameter wires to expand by more than 30% in diameter.

Samples are characterized by X-ray diffraction, magnetization, and electrical resistivity. X-ray diffraction spectra are taken with \( Cu K_\alpha \) radiation in a Scintag diffractometer where the scan angle \( 2\theta \) varies from 20\(^\circ\) to 90\(^\circ\) with a scan step of 0.020\(^\circ\). Magnetization is measured in a Quantum Design \( MPMS - 5 \) magnetometer with a 6 \( cm \) sample travel in a magnetic field of 25 \( Oe \) in a zero-field-cooled mode. Resistivity is measured with a standard four probe technique using an \( LR - 700 \) resistance bridge.
III. RESULTS AND DISCUSSION

The lattice constants of the \( MgB_2 \) phase, determined from X-ray data, change relatively little with time of reaction for powders and have values close to those previously reported.\[1\] The dynamics of the growth of the \( MgB_2 \) phase are illustrated by the study of powder diffraction X-ray data after different times of reaction in Fig. 1. The major \( B \) peak at 38°, marked by the solid line on the figure, is small and goes away during processing. For particle sizes used here (less than 100 \( \mu m \)), the \( MgB_2 \) peaks grow quickly between 30 \( min \) and 60 \( min \) and remain relatively unchanged from 120 \( min \) to 240 \( min \). The \( Si \) peaks used for a standard have been removed from these spectra. It should be noted that when the reaction ampoule was placed in a furnace, heated to 950°\( C \), left for 120 \( min \), and quenched, the powder X-ray spectra showed many second phase peaks. Zero-field-cooled magnetization measurements for these same samples show the transition width narrowing from 15 \( min \) to 30 \( min \) and then remaining relatively constant at about 0.5 \( K \).

Electrical resistivity of the sintered pellets is compared to the wires in Fig. 2. The inset in Fig. 2 shows an expanded view near the transition temperature and indicates values at 40 \( K \) of about 1.5 \( \mu ohm - cm \) for the pellets and 0.4 \( \mu ohm - cm \) for the wire segments. These processing methods give very low electrical resistivity in the normal state for both pellets and wires. Because both the relatively open structure of the pellet and the dense structure of the wire samples have comparable residual resistivity ratios, \( RRR \geq 20 \), we think the lower resistivity values for the wire sample are due to its higher density.

In order to study the synthesis of \( MgB_2 \) wire, a series of exposure time, \( t \), of the boron fibers in \( Mg \) vapor was measured for 15 \( min \) \( \leq t \leq 240 \( min \). For the processing of the 100 \( \mu m \) diameter fibers, the scanning electron micrographs in Fig. 3a and 3b illustrate the behavior seen. In these micrographs, \( Mg \) has a much higher atomic number than \( B \) so the shading is a good indication of \( Mg \) content. In Fig. 3a, a length of fiber reacted for 60 \( min \) has been polished through a section that misses the tungsten-boride core in the middle of the fiber. The \( Mg \) concentration is very high at the outside surface region marked (1), and there is a clear front of \( Mg \) moving across the fiber. At the boundary between the regions marked (2) and (3), energy dispersive X-ray spectra (EDS) show that the \( Mg \) level abruptly falls by about 40%. Region (3) has a fairly high \( Mg \) content, even though it has not transformed to the \( MgB_2 \) phase. As shown by the diameter lines, the diameter of this section has grown by more than 10% from the original 100 \( \mu m \).

A different section of fiber reacted for 60 \( min \) in the same run as in Fig. 3a is shown in Fig. 3b. Here the polishing just barely exposes the tungsten-boride core along the centerline. This SEM micrograph shows many of the common defects. The dark line along the center is a void region, which often occurs near the tungsten-boride core, and an EDS spectrum shows very strong \( W \) lines in this region. The bright region marked (A) is an \( MgB_2 \) region and the dark region marked (B) is an unreacted \( B \) region. If optical pictures are taken, the \( B \) regions stand up above the \( MgB_2 \) regions because they are harder and polish less rapidly. Figure 3c shows an EDS line scan measurement of the \( Mg \) concentration taken along the dark line running from upper left to lower right in the left-center portion of Fig. 3b. The \( Mg \) count on Fig. 3c drops from about 1.4 to about 0.9 going from the bright region to the dark region. The tick mark on the line in Fig. 3b corresponds to the vertical line in Fig. 3c and to a point where the scan moves from a dark region back into a bright region near the
core. Magnesium seems to diffuse very rapidly along the core region and diffuse outward from there to form $MgB_2$. The void region shown by the dark area in the upper left corner of Fig. 3b is unusually large, and the bottom of the void is clearly seen in the SEM. Voids are commonly about $10 - 20 \ \mu m$ across, and the bottom of the void generally can be seen in the SEM. The diagonal regions of high Mg content we believe are cracks where the Mg can diffuse rapidly and start the formation of $MgB_2$.

A $B$ fiber reacted for 30 min is shown in Fig. 4a. Again the polishing depth does not cut through the core. The sample has much less conversion to $MgB_2$, shown by the bright spots. EDS measurements show the highest Mg content in the bright spot marked (C), substantially less Mg near the edge at the point marked (A), and even less at the point near the center marked (B).

Another $B$ fiber reacted for 15 min is shown in Fig. 4b. In the left edge of this fiber, the tungsten core shows through, and the diameter of the fiber is still close to 100 $\mu m$. The EDS data show only a small amount of Mg near the edge of the fiber and practically none in the center of the fiber.

When exposure time, $t = 120 \ \text{min}$, the $100\mu m$ starting diameter fibers are fully reacted and end up having a final diameter of about $160 \ \mu m$. To examine how the process scales with initial fiber size, a $141\mu m$ diameter fiber was exposed for a much longer time, $t = 36 \text{ h}$, with the results shown in Fig. 5. The conversion to $MgB_2$ has increased the diameter of the wire to greater than $180\mu m$, as shown by the diameter measurements. There are no second phase particles large enough to be seen in the SEM micrograph, and the fiber is relatively void free.

**IV. CONCLUSIONS**

Low resistivity, high purity powders and highly dense wires of $MgB_2$ can be synthesized by exposure of boron powder and boron fibers to $Mg$ vapor at 950°C for adequate exposure time. Comparable results are seen for both 100 $\mu m$ and 141 $\mu m$ diameter fibers. For $B$ fibers that are placed in a furnace preheated to 950°C, the $MgB_2$ phase begins to form quickly after about 15 min and is about 50 percent complete after an hour. Diffusion of Mg along the tungsten-boride core and along voids or cracks in the fiber are important means of transport. As the $MgB_2$ phase forms, the diameter of the fiber grows from about $141 \ \mu m$ to about $190 \ \mu m$. As reported earlier, the wire segments provide a highly conducting material with a normal state resistivity of about 0.4 $\mu ohm - cm$ and a superconducting critical current density of about 20,000 $A/cm^2$ at 1 T and 20 K.

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FIG. 1. X-ray spectra for boron powder reacted for different times.
FIG. 2. Comparison of electrical resistivity of a sintered pellet and a reacted wire segment.
FIG. 3. SEM micrograph of two segments of 100 µm diameter boron fibers after 60 min in Mg vapor at 950°C. Fig. 3c is an EDS scan along the line drawn in Fig. 3b.
FIG. 4. SEM micrographs of 100 µm boron fibers reacted for a) 30 min and b) 15 min.
FIG. 5. SEM micrographs of a wire segment for the larger diameter boron fiber that is fully reacted.