Development of Ti-sheathed MgB$_2$ wires with high critical current density

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Abstract

Working towards developing lightweight superconducting magnets for future space and other applications, we have successfully fabricated mono-core Ti-sheathed MgB$_2$ wires by the powder-in-tube method. The wires were characterized by magnetization, electrical resistivity, x-ray diffraction, scanning electron microscopy, and energy dispersive spectrometry measurements. The results indicate that the Ti sheath does not react with the magnesium and boron, and the present wire rolling process can produce MgB$_2$ wires with a superconducting volume fraction of at least 64% in the core. Using the Bean model, it was found that at 5 K, the magnetic critical current densities, $J_c$, measured in magnetic fields of 0, 5, and 8 T are about $4.2 \times 10^5$, $3.6 \times 10^4$, and $1.4 \times 10^4$ A cm$^{-2}$, respectively. At 20 K and 0 T, the magnetic $J_c$ is about $2.4 \times 10^5$ A cm$^{-2}$. These results show that at zero and low fields, the values of the magnetic $J_c$ for Ti-sheathed MgB$_2$ wires are comparable with the best results available for the Fe-sheathed MgB$_2$ wires. At high fields, however, the $J_c$ for Ti-sheathed MgB$_2$ wires appears higher than that for the Fe-sheathed MgB$_2$ wires.

1. Introduction

Large-scale superconducting magnets depend critically on wires with high critical current densities ($J_c$) at temperatures where cryogenic losses are tolerable. The intermetallic superconductor magnesium diboride, MgB$_2$, has emerged as a strong candidate for superconducting tape/wire use under recent developments [1–7]. Its critical transition temperature ($T_c$) is 39 K, allowing for use in liquid hydrogen, which is expected to be widely accessible in the near future. For certain types of application, such as in the growing sector of electric space propulsion, lightweight superconducting magnets are preferred. Lightweight magnets require the use of light metal as the sheath material for MgB$_2$ wires made by the powder-in-tube (PIT) process. The most favourable sheath metal should at least meet the following requirements: (1) having low mass density, (2) having chemical compatibility (being unreactive with MgB$_2$, B, and Mg during the sintering process), (3) being non-magnetic, (4) having appropriate mechanical strength and hardness for cold work (such as wire drawing). In the last five years, much effort has been made towards the fabrication and characterization of PIT MgB$_2$ wires/tapes with different sheath metals, such as iron (Fe), nickel (Ni), copper (Cu), silver (Ag), niobium (Nb), tantalum (Ta) and even aluminium (Al) [3–13]. Among these sheath metals, Fe seems to be the best; with it, a $J_c$ as high as $\sim 3 \times 10^5$ A cm$^{-2}$ [5, 13–16] can be achieved at 5 K and in zero field. The disadvantage of using Fe as the sheath is that it is magnetic and has a large mass density of 7.87 g cm$^{-3}$. Recently, it was reported that some Ta-and Nb-sheathed MgB$_2$ wires can also reach $J_c$ values comparable with that for the Fe-sheathed wires [9], but these metals are more expensive and the mass densities (16.69 g cm$^{-3}$ for Ta and 8.57 g cm$^{-3}$ for Nb) are even higher than that of Fe. As a matter of fact, except Al, all of the above mentioned metals...
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have mass densities greater than that of Fe. For Al, however, since both its mechanical strength and melting temperature (660 °C) are much lower than those of other metals, a high $J_c$ is hard to achieve due to the difficulties in wire drawing and sintering at temperatures higher than the melting point.

Titanium (Ti) seems to be a very promising sheath material for lightweight and high $J_c$ MgB₂ wires due to its very low mass density (4.57 g cm⁻³), excellent chemical stability, non-magnetic nature [17, 18], and high mechanical strength. The major difficulty for Ti is with the cold work for wire rolling or drawing. Very recently, some of us tried to use Ti as the sheath material for fabricating some MgB₂ wires and solved this problem by pre-annealing of the Ti tubing [4]. To our knowledge, no results on magnetic $J_c$, $T_c$, and x-ray diffraction (XRD) patterns for Ti-sheathed MgB₂ wires have been reported yet. In this paper, we present the results on magnetic $J_c$, electrical resistivity, XRD, scanning electron microscopy (SEM), and energy dispersive spectrometry (EDS) measurements for the newly fabricated Ti-sheathed MgB₂ wires.

2. Experimental details

The standard powder-in-tube method was used to fabricate the Ti-sheathed MgB₂ wires. The Ti tubes (supplied by Tico Titanium, nominally 99.85% pure) used in the wire fabrication had an OD of 6.35 mm, wall thickness of 1.65 mm, and length of about 3 inch. Initially, the Ti tube was annealed for about 4 h at 700 °C in order to relieve the stress for cold-working. Mg powder (99.8% purity and ~325 mesh) and amorphous B powder (99.99% purity and ~325 mesh) from Alfa Aesar were stoichiometrically mixed in a glove box filled with argon (Ar). The mixed powder was then milled by a Spex-8000 high energy ball mill for 2 h. Such a ball milling process can reduce the average size of the powder particles from 325 mesh (or 44 μm) to micron or nanometre scale so that more complete reaction and higher grain connectivity in the formed MgB₂ can be achieved. In figure 1, we show the SEM images of the milled mixture of Mg and B powder (in 1:2 ratio). The milled powder is very uniform in size. No particles with diameter greater than 2 μm were found and the diameters for most of the particles are smaller than 1 μm. The big clusters in the images are aggregations of individual particles. These clusters were formed when the powder was pressed onto a double carbon tape for SEM measurement. The mass density of the mixture powder after ball milling was measured to be about 0.79 g cm⁻³.

The milled Mg + 2B powder was then loaded into a Ti tube with one end sealed. This was done in a glove box filled with Ar. The Ti tube was then taken out from the glove box and the remaining end of the tube was mechanically crimped in the air. The powder-filled Ti tube was then drawn into a wire with 1 mm × 1 mm cross-sectional area using a motorized rolling mill with 17 groves. The area of the core for these wires is about 0.126 mm². Wires of about 6 inch were then cut from the as-drawn wire and sintered in a tube furnace in flowing high purity argon with the following schedule: the temperature was ramped up from room temperature to 800 °C at a rate of 300 °C h⁻¹, kept at 800 °C for 30 min, and then cooled down to room temperature at a rate of 100 °C h⁻¹.

The XRD pattern was obtained using a Rigaku x-ray diffractometer with Cu Ka radiation. To get the core materials out of the Ti sheath for making the XRD slide sample, a piece of wire was rolled into thin tape, cut with scissors, and finally peeled off with a knife. The core material was then ground into fine powder for XRD measurement. The SEM and EDS measurements were performed using a JEOL JSM-6330F field emission scanning electron microscope. The temperature ($T$) dependent resistivity was measured by a standard four-probe dc technique in a temperature range of 10–273 K. Electrical contacts were made with Epo-tek H20E silver epoxy. The hysteresis loops of the magnetization ($M$) as a function of the applied magnetic field ($H$) were measured using an Oxford Instruments Maglab 9 T vibrating sample magnetometer (VSM). The ramping rate of the field was fixed at 1 kOe min⁻¹. The data were taken every two seconds, corresponding to a step of magnetic field of $\Delta H \approx 33$ Oe. The wire sample used in the hysteresis loop measurement was 7.5 mm long and placed parallel to the direction of the field. The temperature ($T$) dependent magnetization, $M(T)$, was measured in both zero-field cooled (ZFC) and field cooled (FC) modes in the temperature range of 5 K $\leq T \leq 50$ K using a magnetic properties measuring system (MPMS) magnetometer from Quantum Design. The wire sample for the $M(T)$ measurement was 9.5 mm long and the axial direction of the wire was also parallel to the direction of the applied field. The samples for all of the measurements in this study were cut from the same piece of heat treated Ti-sheathed MgB₂ wire.
3. Results and discussion

Figure 2 shows the powder XRD pattern for the superconducting core material of the Ti-sheathed MgB₂ wire. For comparison with it, in figure 2 we also show the XRD patterns for the commercial MgB₂ and Ti powder (both from Alfa Aesar, -325 mesh). All of the XRD lines in the pattern of the MgB₂ wire can be indexed with the MgB₂ phase except two very weak impurity peaks which can be attributed to the phase of Ti by comparison with the pattern of Ti powder shown in figure 2.

We believe that the Ti impurities were from the Ti sheath during the preparation of the XRD sample slide. When the wire was peeled open and the core material was scraped from the inner wall of the Ti sheath with a knife, some very small pieces of Ti debris from the Ti sheath were stripped away and fell into the powder of the core material. In figure 3, we show the EDS spectrum for the MgB₂ core. In the spectrum, only the Mg and a weak O peak were observed and there was no Ti peak seen. The oxygen content could be from the surface polishing process used in preparing the SEM sample and the crimping of the end of the Ti tubing (in air) in sealing the tubing. The EDS result indicates that the Ti did not react with Mg or B to form any Ti compounds in the core. It also suggests that the Ti impurities observed from the XRD pattern were more probably introduced in the XRD sample preparation process, rather than produced in the wire fabrication process.

The temperature dependent dc magnetic susceptibility, $\chi(T)$, for the Ti-sheathed MgB₂ wire sample is shown in figure 4(a). To obtain the $\chi(T)$ curves, the magnetic moment (m) was measured under both ZFC and FC conditions in an applied field of $H = 20$ Oe, then $\chi(T)$ was calculated...
using the formula $\chi = M/H = m/(V_{\text{geom}}H)$, where $V_{\text{geom}}$ is the geometric volume of the MgB$_2$ core. The size of the MgB$_2$ core has a length of $l \approx 9.5$ mm and a cross-sectional area $A \approx 0.34$ mm $\times$ 0.37 mm = 0.126 mm$^2$, which gives $V_{\text{geom}} = lA \approx 0.012$ cm$^3$. Figure 4(a) shows that the superconducting transition temperature, $T_c$, defined as the onset of diamagnetism, is 36 K. This $T_c$ value is slightly lower than the optimal 39 K but is comparable with the $T_c$ (~35–37 K) reported for some Fe-, Nb-, and Cu-sheathed MgB$_2$ wires [9, 10, 19, 20]. The width of the transition (10%–90% of the full drop in $\chi$) is about 1.5 K. Figure 4(b) shows the temperature dependent resistivity $\rho(T)$ for the sample. The onset $T_c$ is about 36.2 K and the width of the transition (10%–90% of the full drop in $\rho$) is about 1.5 K. These values match well with those observed from the $\chi(T)$ curve in figure 4(a). Above $T_c$, the $\rho(T)$ curve displays a metallic behaviour. Compared with the $\rho(T)$ curves for pure MgB$_2$ samples synthesized by various methods [16, 21], the $\rho(T)$ curve shown in figure 4(b) has less curvature, reflecting a certain contribution to the total resistivity due to the Ti metal sheath.

The $\chi(T)$ curve in the ZFC mode shown in figure 4(a) measures the amount of flux exclusion (or diamagnetic shielding), whereas that in the FC mode measures the flux expulsion (or Meissner effect). The values of $\chi$ at 5 K in the FC and ZFC modes are $\chi_{\text{fc}} = 8.68 \times 10^{-4}$ emu cm$^{-3}$ Oe$^{-1}$ and $\chi_{\text{zfc}} = 5.06 \times 10^{-2}$ emu cm$^{-3}$ Oe$^{-1}$, which correspond to values of $-4\pi \chi_{\text{fc}} = 1.1\%$ and $-4\pi \chi_{\text{zfc}} = 64\%$, respectively. Canfield et al [21] measured $-4\pi \chi_{\text{fc}}$ for a dense MgB$_2$ sample which has a mass density of about 94% of its theoretical value 2.55 g cm$^{-3}$, and they found that the value of $-4\pi \chi_{\text{fc}}$ at 5 K is very close to 100%. Their result suggests that for MgB$_2$ wires, the superconducting volume fraction of the total volume of the core can be estimated as $-4\pi \chi_{\text{fc}}$. Thus, the measured $-4\pi \chi_{\text{fc}}$ value indicates that the superconducting volume fraction in our wire sample is about 64%, corresponding to a mass density of about 1.63 g cm$^{-3}$ (or 64% of 2.55 g cm$^{-3}$). Since the mass density of the Mg + 2B precursor powder mixture after milling is 0.79 g cm$^{-3}$, the mass density of 1.63 g cm$^{-3}$ means that there was a 52% volume reduction during the wire rolling in the wire fabrication process.

The rest of the 36% volume fraction represents the sum of the non-superconducting regions, which include the open holes, voids and any non-superconducting materials in the core. Indeed, the existence of a large number of spherical holes or voids can be directly observed from the SEM images of the cross-section of the polished end of the wire, which are shown in figure 5. The average diameter of these holes/voids is about 1–3 $\mu$m, similar to the size of the Mg powder particles in the milled Mg + 2B powder precursor (see figure 1). Thus, it is very possible that these holes are partially due to the Mg voids produced during the sintering process when some of the Mg particles evaporated and escaped from the ends of the wire. The volume reduction in the Mg + 2B → MgB$_2$ reaction itself could also be a source of the production of the holes/voids. Similar voids were also found to exist in Fe-sheathed MgB$_2$ wires by other groups [8, 22]. We believe that these holes/voids, when connected with the non-superconducting materials existing in the superconducting matrix, can form some kind of ‘effective open holes’ network and result in the very small, observed Meissner effect ($-4\pi \chi_{\text{fc}} = 1.1\%$) under the FC condition. From figures 5(a) and (c), we can see that...
the distribution of the holes/voids in the cross-sectional area of the core is non-uniform. In certain regions where the density of the holes/voids is very high, the superconducting MgB$_2$ grains with size of about 1 $\mu$m can be substantially penetrated by the magnetic field to a depth equal to the London penetration depth $\lambda_{\text{L}}$ ($\sim$110–180 nm) [16]. Thus, the estimated value, 64%, represents only the lower bound estimate for the true superconducting fraction which should be greater than 64%. The difference between $-4\pi\chi_{\text{dc}}$ and $-4\pi\chi_{\text{fc}}$, i.e., $-4\pi(\chi_{\text{dc}} - \chi_{\text{fc}}) \approx 63\%$, is just too big to be explained solely by the volume fraction of the ‘effective open hole’ alone. This large difference of $\chi_{\text{dc}}$ and $\chi_{\text{fc}}$ indicates that there exists a large flux pinning force in the MgB$_2$ core which retains most of the magnetic flux in the core under the FC condition.

Figure 6 shows the magnetization hysteresis loops, $M(H)$, measured at three temperatures, 5, 20, and 30 K, with the maximum sweeping fields of 8 T (or 80 kOe), 4.3 T, and 1.5 T. The $M(H)$ curves measured at 20 and 30 K are full loops but that at 5 K is slightly over a half-loop, i.e., with the field swept from 0 to 8 T and then from 8 to $-8$ T. Since the $M(H)$ loops have inversion symmetry about the origin $(M=0, H=0)$, for the loop measured at 5 K, the magnetic $J_c$ in the field range from 0 to 0.5 T can be estimated by the inversion of the $M(H)$ curve in the field range from 0 to $-0.5$ T. Since the data points were taken with a very small step, i.e., 1/300 T, the plotted $M(H)$ data points in figure 6 for each loop appear to be a continuous curve. The magnetic $J_c(H)$ as a function of field $H$ was determined using the formula $J_c = 20\Delta M/[\mu_0(1-a/3b)]$ [16, 23–25] from the Bean critical state model [26], where $\Delta M$ is the difference between the upper and lower branches of the $M(H)$ curve (in emu cm$^{-3}$); $a \times b$ is the sample’s cross-sectional area perpendicular to the direction of the applied magnetic field with $a < b$, and $a$ and $b$ are in cm; and $J_c$ is in A cm$^{-2}$. For our sample, $a = 0.034$ and $b = 0.037$ mm. For $a = b = d$, this formula reduces to $J_c = 30\Delta M/d$ for a square prism or a cylinder of diameter $d$ [27–29]. In the past, some groups also used the same formula $J_c = 20\Delta M/[\mu_0(1-a/3b)]$ to estimate the $J_c$ values for samples with cross-sectional area of $2a \times 2b$ instead of $a \times b$ [22, 30, 31]. It should be noted that the $J_c$ value obtained in this way would be double that estimated using $a \times b$ as the cross-sectional area. For Ti-sheathed MgB$_2$ wires, there is no contribution to $\Delta M$ or $J_c$ from the Ti sheath due to its paramagnetism [17, 18]. Since the $M(H)$ curve for paramagnetic materials like Ti is reversible, the magnetization backgrounds contained in the upper and lower branches of the $M(H)$ loop are equal and should be cancelled in the subtraction procedure of the $\Delta M$ calculation. Also, since the $\chi$ value of Ti between 4.2 and 70 K is very small ($\sim 3 \times 10^{-6}$ emu g$^{-1}$ [17] or $1.4 \times 10^{-5}$ emu cm$^{-3}$), the effect of the Ti paramagnetism on the $M(H)$ hysteresis loops in figure 6 is negligibly small. Indeed, we have measured the $M(H)$ curve for a piece of Ti-sheathed MgB$_2$ wire at 50 K (above $T_c$) with field varying between 0 and 1.5 T, and confirmed that the $M(H)$ curve was reversible and gave a $\chi$ value of $1.44 \times 10^{-5}$ emu cm$^{-3}$.

Figure 7 shows the dependence of magnetic $J_c$ on the applied magnetic field at the three temperatures 5, 20, and 30 K. At 5 K, the $J_c$ values at fields of 0, 2, 5, and 8 T are about $4.2 \times 10^5$, $1.7 \times 10^5$, $3.6 \times 10^5$, and $1.4 \times 10^5$ A cm$^{-2}$, respectively. At 20 K, the $J_c$ values at fields of 0 and 4 T are about $2.4 \times 10^5$ and $5.0 \times 10^4$ A cm$^{-2}$, respectively. In figure 8, we plot $J_c$ as functions of the temperature at various fields from 0 to 4 T. These results show that at zero and low fields, the values of the magnetic $J_c$ for Ti-sheathed MgB$_2$ wires are comparable with the best results available for the Fe-sheathed MgB$_2$ wires. At high fields, however, the $J_c$ for Ti-sheathed MgB$_2$ wires appears higher than that for the Fe-sheathed MgB$_2$ wires. For example, the magnetic $J_c$ values reported recently by Yeoh et al [14] and Xun et al [15] for undoped Fe-sheathed MgB$_2$ wires are the following: at 5 K, for fields of 2, 5, and 8 T, the magnetic $J_c$ values are, respectively, $\sim 1.7 \times 10^5$, $2 \times 10^5$, and $3 \times 10^4$ A cm$^{-2}$; at 20 K and for fields of 0 and 4 T, the $J_c$ values are $J_c \sim 2.6 \times 10^5$ and $< 3 \times 10^4$ A cm$^{-2}$, respectively. These values are comparable with our $J_c$ values for Ti-sheathed MgB$_2$ wire at low fields but substantially lower at higher fields. The magnetic $J_c$ values measured in the present study show that the fabrication technique we developed can be used for fabricating high $J_c$ Ti-sheathed MgB$_2$ wires.
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for future lightweight superconducting magnet applications. It is highly possible that the $J_c$ for the Ti-sheathed MgB₂ wires could be further increased by several routes such as improving the wire drawing process, reducing the size of the precursor particles, doping with other elements or compounds as pinning centres, optimizing the sintering temperature and time, and reducing the number of holes/voids by sealing the ends of the wires before sintering.

4. Conclusions

We have successfully fabricated mono-core Ti-sheathed MgB₂ wires by the PIT method. The wire samples were characterized by magnetization, electrical resistivity, XRD, SEM, and EDS measurements. It was found that at 5 K, the $J_c$ values at fields of 0, 2, 5, and 8 T are about $4.2 \times 10^5$, $1.7 \times 10^5$, $3.6 \times 10^5$, and $1.4 \times 10^5$ A cm⁻², respectively. The $J_c$ values at 20 K and at fields of 0 and 4 T are about $2.4 \times 10^5$ and $5.0 \times 10^4$ A cm⁻², respectively. Compared with the magnetic $J_c$ reported for similar Fe-sheathed MgB₂ wires, the magnetic $J_c$ for Ti-sheathed wires is comparable at low fields but higher at high fields (above 4 T). The $T_c$ was found to be about 36 K from both the magnetization and resistivity measurements. It appears that the Ti sheath does not react with the magnesium and boron. The ZFC magnetization result indicates that the superconducting volume fraction in the core of the wires is above 64%.

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