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Progress in MgB₂ Superconductor Wires and Tapes

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Abstract

We report on the progress that has been made in developing MgB₂ superconducting wires and tapes for commercialization and research efforts. A number of techniques have been developed to overcome the obstacle posed by the poor critical current density (J_c) of pristine MgB₂. Chemical doping has proved to be the effective way to modify and enhance the superconducting properties, such as the J_c and the irreversibility field (B_{irr}). More than 100 different types of dopants have been investigated over the past 8 years. Among these, the most effective dopants have been identified to be SiC and malic acid ($C_4H_6O_5$). The best results, viz. a B_{irr} of 22 T and J_c of 30,000 A·cm⁻² at 4.2 K and 10 T, were reported for malic acid doped MgB₂ wires, which matched the benchmark performance of commercial low temperature superconductor wires. In this work, we discuss the progress made in MgB₂ conductors over the past few years at the University of Wollongong, Hyper Tech Research, Inc., and Ohio State University.

Keywords : AC loss, CTFF, In-situ, Joint, Magnet, MgB2, Malic acid, MRI, SiC

I. Introduction

The discovery of superconductivity at 39 K in a relatively common material, MgB₂, has triggered a great deal of interest in the research community. The importance of MgB₂ lies in its simple crystal structure, high critical temperature (T_c), high critical current (J_c), large coherence length, and transparency of the grain boundaries to current flow. These properties of MgB₂ offer the promise of important

large-scale and electronic device applications. In particular, using MgB₂ conductors will open up a new domain of applications for superconducting magnets, especially below 5 T and 20 K, as can be seen in figure 1. During the past 8 years, MgB₂ has been fabricated in various forms, including single crystals, bulk, thin films, tapes, and wires [1]. In particular, much effort has been made to improve the J_c value and obtain a greater understanding of MgB₂ as high as 10,000 A·cm⁻² at 10 T and 4.2 K, and 10,000 A·cm⁻² at 5 T and 20 K [3]. This provides proof that the performance of MgB₂ conductors can rival and

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even exceed that of conventional low temperature superconductors (LTS). However, the J_c value of pristine MgB₂ drops rapidly with increasing magnetic field, due to its low upper critical field (B_{c2}) and weak pinning strength. To take advantage of its higher T_c of 39 K, the enhancement of the B_{c2} value and the improvement of the flux pinning are essential. Attempts to enhance the B_{c2} value and flux pinning have been made using a number of techniques, including addition, substitution, and various thermomechanical processing techniques [2-5]. In this article, we give a brief review of our research activities at the University of Wollongong (UoW), Hyper Tech Research Incorporated (HTR), and Ohio State University (OSU) into the materials processing and characterization of superconducting MgB₂ conductors.

II. Continuous tube forming and filling (CTFF)

Continuous tube forming and filling (CTFF), shown schematically in figure 2, is a novel technique for the preparation of MgB_2 conductors. This technique was developed by Hypertech Research Inc. (HTR) in the US to prepare MgB_2 wires and tapes. In this technique, continuous metal strips (Nb, Fe, etc.) were first produced as an inner material. As the ribbon enters and moves through the tube shaping dies, they gradually form it into a U shape. After the composite powder (99.9 % Mg and 99.8 % B) is inserted, the closing dies gradually close off the tube. After the tube has been closed, it passes through subsequent dies to reduce the diameter to a fine wire. Numerous long lengths of wire have been made using this technique.

So far, HTR has 8 years of manufacturing development experience with MgB₂ composite conductors. This conductor was designed with its manufacturability in mind. The processing steps are of the commercial variety. Aside from HTR's CTFF technique, which is particularly advantageous for forming strands with much longer lengths, no specialty wire drawing steps are required. HTR regularly manufactures composites with lengths of over 30 km. Longer lengths could also be produced and we are presently working on integrating these strands into appropriate applications. The strands are basically made from in-situ powders, and the strands have Nb or Fe barriers, Cu stabilizers, or Cu-Ni outer sheaths (called "Monel") with different filament numbers from 7 to 61 in the final multi-filamentary Heat treatment (HT) is typically conductor. performed at a temperature of the order of 700 °C for 20 to 40 minutes. For react-and-wind wire, S-glass braid is normally coated on the surface of the conductor as an insulator.



Fig. 1. Comparison of B_{c2} values of low temperature superconductors (Nb-Ti and Nb₃Sn) and MgB₂.



Fig. 2. Schematic of CTFF process.

III. Effects of amorphous and semi-crystalline boron powders

Figure 3 shows a comparison of the J_c values in the MgB₂ monofilament wires made from different boron powders with amorphous and semi-crystalline phases. As can be seen in the figure, the J_c values of the wires made from 99.8 % amorphous boron showed the best performance. Quite interestingly, the J_c values for the wires made from semi-crystalline boron powders supplied by both the SMI and Tangshan companies were quite poor under a high magnetic field. The J_c was estimated to be below 1,000 A·cm⁻² at 10 T and 4.2 K. However, the J_c of the wires made from amorphous boron may well cross over that of the wires made from semi-crystalline boron in the low-field region. This indicates that wire conductors made from semi-crystalline boron can be applied in a magnet system operated at 1-2 T for greater economy and that an un-doped sample with good quality can be equally useful and cost-effective as a doped one.

IV. Chemical doping: malic acid

IV-I. Critical current density

Our persistent attempts to increase the performance



Fig. 3. Comparison of J_c values in MgB₂ wires made from different boron powders with amorphous and semicrystalline phases.

of MgB₂ wires over the past few years are summarized in figure 4. Stoichiometric binary MgB₂ wires with various sheath materials were the first to be fabricated. Then, wires with 10 % excess Mg plus SiC dopant (Mg₁₁B₂-SiC), 15 % excess Mg only (Mg₁₁₅B₂), and 15% excess Mg plus SiC dopant (Mg_{1.15}B₂-SiC) were introduced. However, the best J_c was limited to 100,000 A·cm⁻² and 10,000 A·cm⁻² at 6 T and 11.5 T, respectively. Currently, the J_c values obtained with malic acid doping are as high as 100,000 A·cm⁻² at 6.8 T and 10,000 Acm⁻² at 11.7 T, which are comparable to those of commercial Nb-Ti wires. The critical current density is about 25,300 A·cm⁻² at 4.2 K and 10 T. Interestingly enough, the crossover of the critical current densities between the un-doped and malic acid $(C_4H_6O_5)$ doped wires appear at around 2 T. On the other hand, the crossover between the un-doped and SiC samples appears at around 4.5 T. This is due to the large fraction of impurity phases, such as Mg₂Si, MgO, and Si for the SiC doped MgB₂. However, much more research into malic acid doped wires is still needed before they can be used in real applications. To address this issue, recently, cold high pressure densification has been suggested as an alternative way to enhance the mass density after cold high



Fig. 4. Comparison of J_c -*B* characteristics at 4.2 K of malic acid doped wire with those of other commercial MgB₂ wires fabricated by Hyper Tech Research. The malic acid doped MgB₂ wire was sintered at 600 °C for 4 hours. The critical current density was about 25,300 Acm⁻² at 4.2 K and 10 T.

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pressure deformation (CHPD) [5]. The J_c value at 4.2 K and 10 T was reportedly further increased to ~40,000 A·cm⁻² for a malic acid doped square conductor sintered at 600 °C for 4 hours. This is the best performance reported so far for an in-situ processed conductor.

IV-II. N-value

In particular, the *n*-value of a conductor is a parameter that plays an important role in the prediction of its decay properties in a magnetic field. Here, the *n*-values were determined from the slope in the plot of log *E* versus log *J* in the *E* range from 0.1 to 10 μ V·cm⁻¹ based on the power law, $E_c = E(V/V_c)^n$. For a magnet operated in persistent current mode, the behavior of the current decay, *i*, can be expressed by [6]

$$i = \left\{ \left(i_0^{1-n} + \frac{E_c \cdot l}{R \cdot i_c^n} \right) e^{(n-1)\frac{R}{L}t} - \frac{E_c \cdot l}{R \cdot i_c^n} \right\}^{\frac{1}{1-n}}$$
(1)

where *R* is the joint resistance, *n* is the *n*-value, and *L* and *l* are the inductance and total length of the magnet, respectively. In addition, E_c is the critical electric field, i_c is the critical current, and i_0 is the initial current. As shown in equation (1), the current decay strongly depends on the *n*-value and joint



Fig. 5. Magnetic field dependence of n-value for un-doped and malic acid doped MgB₂ conductors at 4.2 and 20 K.

resistance. When a conductor with a high *n*-value is used as the magnet material, the associated resistance component can be effectively reduced. It is well known that a high quality sample shows a high *n*-value. It is thus essential to fabricate an MgB₂ conductor with a highly uniform microstructure, in order to reduce the dissipation for magnet applications in persistent mode operation. Figure 5 shows the magnetic field dependence of the *n*-value for the un-doped and malic acid doped MgB₂ conductors at 4.2 and 20 K.

V. Development of MgB₂ conductors

The commercial multi-filament wires fabricated by HTR consisted of 18 monofilaments with Nb/Cu/ Monel sheaths + 1 center copper wire. So far, a number of experimental strands have been developed for different application fields. Recently, HTR fabricated a multi-filamentary conductor with seven small fine filaments, each with a diameter of approximately 15-20 µm. For the purpose of increasing the ductility and stability of the strand, the Monel outer sheath was replaced by oxide-dispersion strengthened (ODS) copper, with the trade name Glidcop[™]. This ODS sheath offers the benefits of lower resistivity while retaining sufficient strength to support mechanical deformation, especially in the drawing process. In addition, conductors with high filament counts have been made. Figure 6 shows the cross-sectional views of the different conductors.

VI. Target application: MRI

 MgB_2 conductors have various advantages in magnetic resonance imaging (MRI) applications [7]: (1) respectable properties for low to mid-field magnets operating at temperatures as high as 20 K, (2) wire manufacturing no more difficult than for Nb-Ti wire, (3) Mg and B are lower cost raw materials than Nb and Ti, (4) MgB₂ has 1/3 the density of Nb-Ti, so the same number of kg of the

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Fig. 6. Cross-sectional views of multifilamentary wires: (a) wire with small fine filaments, (b) $\text{Glidcop}^{\text{TM}}$ wire, and (c) high filament count wire.

raw material will yield three times the piece length, (4) a faster charging rate compared to Nb-Ti based magnets, and (5) its high T_c offers a larger thermal margin than the value of 9 K for Nb-Ti. The Massachusetts Institute of Technology (MIT), one of the collaborators, constructed an MRI demonstration coil, which is shown in figure 7. The operating current of 88 A in the test coil set generated a central bore field of 0.54 T at 14 K [8]. It used an MgB₂ conductor with a length of 10 km for the demonstration.



Fig. 7. Demonstration coil of MgB₂ MRI at MIT.

VII. Next steps

VII–I. Joints

MRI superconducting magnets are currently based on Nb-Ti operated in persistent mode, which is made possible by a so-called "superconducting joint". Even though a superconducting joint for MgB₂ conductors was reported by Hitachi in 2005, the performance presented by its joint resistance and field stability was not as good as that in persistent mode with LTS [9]. In addition, the joint was between Nb-Ti and MgB₂, thereby limiting its operation to temperatures above 10 K. For MgB₂ magnets operated in persistent mode at 15-20 K, a joint with only MgB₂ conductor needs to be developed. Iwasa et al. [10] also reported the successful development of a superconducting joint with un-reacted conductors on the laboratory scale. Very recently, Giunchi et al. [11] showed positive results based on Mg diffusion processing with ex-situ processed wires.

VII-II. AC loss

Attempts to determine the alternating current (AC) loss of MgB_2 conductors have recently begun [12]. Most superconducting devices operate on AC, and the few applications that were DC powered involved some AC ripple or ramping up and down. AC losses are an issue in power system design. The total AC losses consist of hysteretic, coupling, and eddy current components. Hysteretic losses can be reduced by using the proper filament size. Lower ferromagnetic

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losses can be achieved by replacing Monel with ODS Cu. In addition, the coupling losses can be minimized by braiding and twisting. Finally, the coupling eddy current losses can be reduced by increasing the matrix resistivity. What is important is that MgB₂ wires are superior to tape conductors from the viewpoint of the AC losses.

VII-III. Boron powder quality

The possibility and cost effectiveness of fabricating high performance conductors using low grade boron (95-97 %) with crystalline phase has already been demonstrated [13]. Recently, much more attention has been paid to the characterization of the various types of boron powders, because of the limited availability of high quality raw materials. So far, using high purity amorphous boron gives the best J_c performance in a magnetic field. Therefore, to overcome the problem posed by this shortage of high quality raw materials, the ball-milling process is one of the most promising means to purify the crystalline phase. The samples fabricated by ball milling had relatively small grain sizes, resulting in the strong field dependence of the J_c value in the high field region. On the other hand, the ball-milled boron exhibited poor connectivity between adjacent grains. It was clearly shown that the observed reduction in the J_c value in the low field region is related to the reduction in the superconducting area fraction (A_F) , which is reflected by the connectivity factor. Even if high temperature sintering is employed to compensate for the degradation of the J_c in the low field region, the consequent grain growth results in the degradation of J_c in the high field region.

VIII. Summary

Significant progress has been made in the development of MgB₂ superconductor conductors for different application fields. However, due to the poor performance of pristine MgB₂ in terms of the critical current density (J_c) and upper critical field (B_{c2}), a number of techniques and dopants have been

employed in an attempt to overcome these problems. According to a recent report [6], the J_c values for malic acid doped MgB₂ conductors are as high as 10,000 Acm⁻² at 10 T and 4.2 K, and 10,000 Acm⁻² at 5 T and 20 K This provides proof that the performance of MgB₂ conductors can rival and exceed that of conventional low temperature superconductors such as Nb-Ti. The on-going research projects at the University of Wollongong, Hyper Tech Research Inc., and Ohio State University will be increasingly directed toward commercial applications.

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