A New Approach to MgB₂ Superconducting Magnet Fabrication

A Miyazoe¹, H Abe², T Ando¹, N Hirota², M Sekino³ and H Wada¹

¹Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba, 277-8561, Japan
²National Institute for Materials Science, Tsukuba, Ibaraki, 305-0047, Japan
³Department of Advanced Energy, University of Tokyo, Kashiwa, Chiba, 277-8561, Japan

E-mail: kk66149@mail.ecc.u-tokyo.ac.jp

Abstract. Fabrication of MgB₂-based superconducting magnets has been attempted by a new approach using film coated on symmetric tubes. Superconducting MgB₂ films have been prepared on iron substrates by electroplating in molten electrolytes. The critical current (Ic) of the MgB₂ electroplating films at 4.2 K and at self-field was 15 A on the basis of 1 μV/cm of Ic criterion. A model calculation has shown that MgB₂-based superconducting magnets based on MgB₂ electroplating films have the potential to generate magnetic fields over 0.5 T.

1. Introduction

The demand for superconducting magnets generating high magnetic fields is increasing in the various applications of superconductivity, such as magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR) spectrometers or nuclear fusion reactors. The next-generation MRI requires superconducting magnets to generate steady magnetic fields over 10 T [1]. In the case of the next-generation NMR spectrometers, steady magnetic fields over 23.5 T are needed [2].

Superconducting magnets are currently made by winding kilometer-long superconducting wires. NbTi and Nb₂Sn are the two most widely used superconductors for kilometer-long superconducting wires. However, it is difficult for NbTi- or Nb₂Sn-based superconducting magnets to generate magnetic fields over 22 T [3]. Furthermore, superconducting magnets using NbTi- or Nb₂Sn-based wires are operated at 4.2 K or below because of their low superconducting transition temperatures (Tc). In order to fabricate superconducting magnets generating high magnetic fields and/or operating at higher temperatures, we need to shift from NbTi or Nb₂Sn to other materials with higher Tc or higher upper critical fields (Hc2) including MgB₂ [4], Nb₃Al [5], YBa₂Cu₃O₇-δ (YBCO) [6], Bi₂Sr₂CaCu₂O₈ or Bi₂Sr₂Ca₂Cu₃O₁₀ (BSCCO) [7]. However, superconducting magnets based on these materials have not been put into practice mainly due to the difficulty in making kilometer-long wires with homogeneous performances over the entire length.

We propose a new approach to fabricating superconducting magnets based on superconductors other than NbTi and Nb₂Sn. This new approach does not include either fabricating or winding kilometer-long wires. Firstly, single-layer coils with diameters of D are made by preparing films of the desired superconductors on cylindrical substrates in such a manner that the superconducting films form helical patterns along the axis of the substrates. Secondly, the single-layer coils with different D
are nested inside one another to make a multi-layer superconducting magnet. This method is named the $\pi D$ method in terms of making superconducting magnets by assembling single-layer coils with diameters of $D$ instead of winding wires with the length of $\pi D$. Details of this method will be described elsewhere [8].

In order to explore the feasibility of the $\pi D$ method, we have attempted to fabricate superconducting coils of MgB$_2$. MgB$_2$ has the highest $T_c$ among intermetallic superconductors ($T_c = 39$ K) [4]. The $H_{c2}$ at 4.2 K of SiC-doped MgB$_2$ is 33 T [9], which is much higher than those of either NbTi or Nb$_3$Sn [10]. MgB$_2$ is a promising material for superconducting magnets generating high steady magnetic fields.

Figure 1 is the schematic diagram of making MgB$_2$-based superconducting magnets based on the $\pi D$ method. Single-layer coils are made by electroplating MgB$_2$ films onto cylindrical substrates. The cylindrical substrates are helically patterned prior to electroplating so as to act as a template for MgB$_2$ films to be electroplated (1, 2). The helical pattern is made by etching the surface of the cylindrical substrate that is previously coated with a resist film. The detail of the patterning process will be described elsewhere. The single-layer coils are assembled into a multi-layer MgB$_2$ superconducting magnet (3).

![Figure 1. Schematic diagram of the $\pi D$ method for making MgB$_2$-based superconducting magnets](image)

2. Experimental

MgB$_2$ films were electroplated onto pure iron plates in molten electrolyte according to literature [11]. The electrolyte consisted of MgCl$_2$ (99.9% purity, Kojundo Chemical Laboratory), KCl (99% purity, Kojundo Chemical Laboratory), NaCl (99.0% purity, Sigma-Aldrich) and MgB$_2$O$_4$ (Kishida Chemical Co.) with a molar ratio of 10: 5: 5: 0.1-0.2. The hygroscopic material, MgB$_2$O$_4$, was dried by heating at 200°C in air for 160 h. The total amount of the electrolytes was approximately 510 g. The electrolyte was always treated in a high-purity Ar (99.9999% purity, Suzuki Shokan) atmosphere. The electrolyte was melted at 600°C in a flow of high-purity Ar gas at 2 l/min and were continuously stirred with a graphite stirrer.

To explore the electroplating condition, cyclic voltammetry (CV) measurements were performed using a potentiostat (Hokuto denko Co.). Graphite rods with a diameter of 1.0 mm (IG-110, Toyo Tanso Co.) were used as the counter electrode (CE). Platinum wires with a diameter of 1.0 mm (99.98% purity, The Nilaco corporation) were used as the reference electrode (RE). Pure iron plates (99.5% purity, The Nilaco corporation) were used as the working electrode (WE). The potential of WE versus RE was scanned in the range from -0.3 V to -1.6 V. Scanning rate was 6.4 mV/s. Electrodeposition was performed at two different potentials of WE, -1.56 and -0.70 V, for a duration...
of 10 min. X-ray diffraction (XRD; Cu-Kα radiation, λ = 0.1540562 nm) was performed using an X-ray diffractometer (RINT-ULTIMA3, Rigaku Co.) in order to identify the precipitates on WE.

Pure iron plates with the width, length and thickness of 10, 50, and 0.5 mm, respectively, were used as the cathodes for electroplating. Graphite rods with a diameter of 1.0 mm were used as the anodes. Two different pretreatments were applied to enhance the adhesion of the electroplating films to iron substrates. 1. Iron substrates were coated with boric acid by dipping into saturated solutions of boric acid (4.8 wt% in water) and dried well in air prior to electroplating. 2. Anhydrous Mg(OH)₂ (99.99% purity, Kojundo Chemical Laboratory) with the molar ratio of 0.0015 relative to MgCl₂ was doped to the electrolyte. In the latter case, iron substrates were not coated with boric acid.

Electroplating was performed in the molten electrolyte by applying a DC potential of 4.0 V between the iron substrates and the graphite anodes for a duration of 10 min. The iron substrates were removed out of the molten electrolyte and were washed in dry methanol (99.8% purity, Nacalai tesque) using an ultrasonic washer to remove the electrolytes. The iron substrates were coated with black electroplating films.

Measurements of critical currents (I_c) of the electroplating films were performed at 4.2 K in liquid He and at steady magnetic fields from 0.0 up to 4.5 T using a superconducting magnet (JASTEC). The current leads were soldered on the iron substrates. Gold wires with diameters of 50 μm (99.95% purity, The Nilaco Co.) were connected to the surface of the electroplating films as voltage taps.

3. Results and discussion

Figure 2 shows the result of CV measurements in the molten electrolyte. On the forward scan of the potential of WE (V_w) from -0.3 V to -1.0 V, the current monotonously decreases from 0 to -56 mA. The current shows a steep drop at V_w = -1.36 V and linearly decreases until it reaches -415 mA at -1.6 V. The steep increase in the amplitude of the current at -1.36 V indicates that electroreduction occurs on WE at the critical potential of V_c = -1.36 V or below. On the backward sweep from -1.6 V, the current monotonously increases and shows a large, broad peak at V_w = -1.0 V. The current steeply converges to zero when V_w exceeds -1.0 V. The large peak on the backward scan is attributed to the decomposition of the precipitates on WE that were formed on the forward scan when V_w < V_c.

Figure 3 presents the XRD profile of the precipitates electrodeposited at a potential below V_c, V_w = -1.56 V, onto the surface of WE. The 110, 200 and 211 reflections of Fe WE are recognized at 2θ = 44.7, 65.0 and 82.3 degrees, respectively. The peaks at 36.9, 42.9 and 62.3 degrees are assigned to the 111, 200 and 220 reflections of MgO. The red curve in the inset shows an enlarged XRD profile near the 200 reflection of MgO at 2θ = 42.9 degrees. The XRD profile is apparently not symmetrical around the peak position of the 200 reflection of MgO. This indicates that the 101 reflection of MgB₂ is superimposed on the 200 reflection of MgO. In contrast, XRD of the precipitates electrodeposited on the WE at V_w = -0.7 V > V_c (see the blue profile) shows only the existence of MgO. Note that the potential of WE relative to CE is near -3.5 V when V_w = V_c. We conclude, therefore, that the potential of WE relative to CE should be kept lower than -3.5 V during electroplating in order to obtain electroplating films that contain MgB₂.
Figure 2. CV profile in the molten electrolyte.
The arrows show the scan directions of the potential of the working electrode.

Figure 3. XRD profiles of the precipitates electrodeposited onto the working electrode at $V_w < V_c$. (red curve)
The blue curve represents the XRD profile of the precipitate obtained at $V_w > V_c$.
The inset shows the XRD profiles expanded.

Figure 4 shows the current-electric field profiles at 4.2 K of a pure iron substrate and of a film electroplated in the electrolyte containing Mg(OH)$_2$. The electric field ($E$) shows a linear dependence on the current ($I$) in the case of the pure iron substrate. In the case of the MgB$_2$-electroplating film, in contrast, $E$ remains near zero until $I$ reaches 15 A. As $I$ increases from 15 A to 25.8 A, $E$ increases moderately. When $I$ reaches 25.8 A, $E$ steeply increases. The critical current ($I_c$) of the MgB$_2$-electroplating film is evaluated to be 15 A on the basis of $E = 1 \mu V/cm$ of $I_c$ criterion.
Figure 4. *I*-*$E$ curves of a pure iron substrate and a MgB$_2$ film electroplated in the electrolytes containing Mg(OH)$_2$. The red open circles and the blue closed squares correspond to the pure iron substrate and MgB$_2$ film, respectively. The inset shows a picture of the MgB$_2$ film electroplated onto an iron substrate.

A simulation was carried out to evaluate the possible performance of the superconducting magnets based on the MgB$_2$-electroplating films on iron substrates. The model specifications of the multi-layer MgB$_2$-based superconducting magnet are as follows: the height, thickness and number of turns of each single-layer coil are 1,000 mm, 0.11 mm and 100, respectively. The width and the thickness of the MgB$_2$-electroplating film are 10 mm and 10 $\mu$m, respectively. 9.1% of the cross section of the multi-layer superconducting magnet is occupied by the MgB$_2$-electroplating films. The diameter of the innermost single-layer coil is 10 mm. The number of single-layer coils that are involved in the multi-layer magnet is 510. Figure 5 shows the calculated load line for the multi-layer superconducting magnet (red closed circles) and critical current densities ($J_c$) of the film (blue open squares) as functions of magnetic fields. The red and blue curves cross at 0.52 T. Therefore, the maximum magnetic field that the multi-layer superconducting magnet can generate is roughly estimated to be 0.52 T.
Figure 5. Load line of the simulated multi-layer magnet (red closed circle) and critical current densities of the MgB$_2$-electroplating film as functions of magnetic fields (blue open square).

4. Conclusion
In this study, we have electroplated superconducting MgB$_2$ films onto iron plate substrates to explore their superconducting performance in terms of a newly developed magnet fabrication method named the $\pi D$ method. Transport measurements have shown that the MgB$_2$-electroplating films on iron substrates possess critical currents over 15 A at 4.2 K and at self-field. A model calculation has indicated that the superconducting magnets based on such MgB$_2$-electroplating films have the possibility of generating the maximum magnetic fields of 0.52 T. The maximum magnetic fields may be improved by optimizing the electroplating conditions. We conclude that the $\pi D$ method, in combination with electroplating, can be a promising approach to fabricating MgB$_2$-based superconducting magnets without making long-sized MgB$_2$ superconducting wires.

5. Acknowledgement
The authors would like to thank Dr. Itoh and Dr. Nimir in National Institute for Materials Science and Dr. Ozaki in Kobe Steel Group for helpful suggestions and discussion.

References
[1] Wada H and Ikehira H 2007 J. Cryo. Soc. Jpn 42 180
[2] Konstantin P, Roland R, Gehard W and Kurt W 1997 Proc. Natl. Acad. Sci. USA 94 12366
[3] Wada H and Kiyoshi T 2002 IEEE Trans. Appl. Superconduct. 12 715
[4] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Nature 410 63
[5] Wood A E, Compton B V, Matthias T B and Corenzwit E 1958 Acta Cryst. 11 604
[6] Wu K M, Ashburn R J, Trong J C, Hor H P, Meng L R, Gao L, Huang J Z, Wang Q Y, and Chu W C 1987 Physic. Rev. Lett. 58 908
[7] Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 Jpn. J. Appl. Phys. 27 L209
[8] Ando T etal. in preparation
[9] Sumption M D, Bhattia M, Rindfleisch M, Tomsic M, Soltantian S, Dou S X and Collings E W 2005 Appl. Phys. Lett. 86 092507
[10] Vinod K, Abhilash G R and Syamaprasad U 2007 Supercond. Sci. Technol. 20 R1
[11] Abe H, Yoshii K, Nishida K, Imai M and Kitazawa H 2005 J. Phys. Chem. Solids 66 406