Superconductivity and Thermal Property of MgB$_2$/Aluminum Matrix Composite Materials Fabricated by 3-Dimensional Penetration Casting Method*\(^1\)

Kenji Matsuda\(^1\),*\(^2\), Tomoaki Saeki\(^1\),*\(^3\), Katsuhiko Nishimura\(^1\), Susumu Ikeno\(^1\), Yukinobu Yabumoto\(^2\) and Katsunori Mori\(^1\)

1 Department of Materials Science and Engineering, Faculty of Engineering, University of Toyama, Toyama 930-8555, Japan
2 Shin-Nikkei Co., Ltd., Funabashi 274-8530, Japan

Superconductive MgB$_2$/Al composite material with low and high volume fractions of particles were fabricated by our special pre-packing technique and 3-dimensional penetration casting method. The composite material showed homogeneous distribution of MgB$_2$ particles in the Al-matrix with neither any aggregation of particles nor defects such as cracks or cavities. The critical temperature of superconducting transition \(T_C\) was determined by electrical resistivity and magnetization to be about 37–39 K. Specific heat measurements further supported these \(T_C\) findings. The Meissner effect was also verified in the liquid He, in which a piece of the composite floated above a permanent magnet. The thermal conductivity of the MgB$_2$/Al composite material was about 25 W/K•m at 30 K, a value much higher than those found for NbTi or Nb$_3$Sn superconducting wires normally used in practice, which are 0.5 and 0.2 W/K•m at 10 K, respectively. A billet of the superconducting material was successfully hot-extruded, forming a rod. The same as the billet sample, the rod showed an onset \(T_C\) of electrical resistivity of 39 K.

*(Received December 8, 2005; Accepted February 8, 2006; Published April 15, 2006)

**Keywords**: composite material, magnesium diboride, aluminum, superconductivity, thermal conductivity, extrusion

1. Introduction

As has been known, MgB$_2$ is the Type II superconductor, and its superconducting transition temperature \(T_C\) is 39 K.\(^3\) Studies on MgB$_2$ has focused on application for superconducting magnets as well as Nb-based intermetallic compounds,\(^2\) and many projects for fabrication of wires and/or sheets are actively being pursued.\(^5\) Superconducting magnets using Nb-based intermetallic compounds have a problem involving quenching.\(^8\)–\(^10\) For example, when the cryocooling system of a magnet is stopped while the transport current is set to about 100 A and the superconducting state is broken, NbTi produces much heat and a superconducting magnet is likely to explode, because NbTi is also an exothermal material and has a higher resistivity in the normal conductive state.\(^9\) Thermal conductivity is also important for superconducting magnets and this problem is common to medical magnetic-resonance imaging (MRI) systems and linear motor trains.\(^10\) To solve this problem, the conventional superconducting wire using Nb$_3$Sn intermetallic compound is combined with copper which has good thermal conductivity.\(^3\)

In our previous studies, we fabricated composite materials formed from Al or age-hardenable Al alloys matrix reinforced by ceramics particles such as Al$_2$O$_3$, SiC, and TiC, and investigated their hardening behaviors, microstructures, and aging properties.\(^11\)–\(^13\) Our special technique for fabricating composite materials can disperse particles in the matrix homogenously without any aggregation and control their volume fractions within the range of 4–40%, even when particle size is less than 1 \(\mu\)m. Thus, these composite materials can be processed by machining, extrusion and rolling.

In the present work, we applied our technique to fabricate billets of composite materials consisting of Al matrix reinforced by MgB$_2$ particles, and evaluated superconductivity and thermal properties. This billet was successfully extruded to obtain a rod.

2. Experimental Procedure

2.1 Sample preparation

MgB$_2$ powders used were provided by Kojundo Chemical Laboratory Co., Ltd., and had purity higher than 99%, and size was smaller than 40 \(\mu\)m. Received powders were gently ground in an agate mortar to break any aggregation. The method for forming a composite material billet was almost the same as that employed in our previous study.\(^11\) Namely, first of all, MgB$_2$ powders were placed in a steel mold, and pressed, thereby forming a preform of compacted powders measuring 30 mm in diameter and 42 mm in length. This preform was set in the bottom of steel mold which was heated about 1073 K. Molten Al at about 1173 K was poured in to this steel mold, a graphite disc was placed on a molten Al, and the molten Al was pressed into the preform via the graphite disc, by means of a pressing machine. By this method, the molten Al can penetrate into the preform from all directions. We refer to this method as the 3-dimensional penetration casting (3DPC) method. After cooling, the billet was removed from the steel mold by cutting. The volume fraction \(V_f\) of MgB$_2$ powders in the obtained billet was about 40%; this sample is referred to as the high \(V_f\) sample. For evaluating the effect of varying \(V_f\), a sample of low \(V_f\) was also fabricated by means of the melt spray method.\(^12\),\(^13\) In this method, MgB$_2$ powders were merely set on the bottom of a steel mold, and molten Al was pressed into this mold through a small aperture. This small aperture produces a jet flow of molten Al, which strongly stirred the powders. After several seconds of stirring, the steel mold was cooled from
only the bottom side through a water jacket, and powders were homogeneously dispersed in the matrix. $V_f$ can be controlled from 4–10%. The billet formed by this method is referred to as the low $V_f$ sample, and its $V_f$ is about 10%. The obtained billet was also extruded by a hot-extruding machine to a 10 mm $\phi$ rod, and the range of extrusion temperature was 723–773 K.

2.2 Measurement of superconductivity and thermal property

Superconductivity and thermal properties were measured by means of Physical Property Measurement system (PPMS, Quantum Design, Co., Ltd.). Samples for these measurements were cut from composite material billets to 1 mm cubes. Electrical resistivity was measured by a DC 4-terminal method, at a direct current of 1.0 mA. The range of temperature employed for measurement of electrical resistivity, thermal conductivity, and magnetization was from room temperature to 4.2 K, and cooling rate was 0.003 K/s. Magnetization was measured by SQUID (Quantum Design, Co., Ltd.) using an applied magnetic field of 100 G. The high $V_f$ sample was confirmed to exhibit the Meissner effect in liquid He. A double glass vessel was used, with the inner being filled with liquid helium and the outer vessel with liquid nitrogen. A permanent Nd magnet was set on the bottom of the inner vessel, and the composite material was gently placed in the inner vessel. The Meissner effect was confirmed by the floating of the composite material above a permanent magnet.

2.3 Microstructures

The microstructures of composite materials were observed by a scanning electron microscope (SEM). Samples for microstructure were simply cut from composite materials and polished using conventional polishing papers. The SEM used was S-3500H (Hitachi, Co., Ltd.) operating at 20 kV, and Mg and Al maps were obtained from a sample by energy dispersive X-ray spectroscopy (EDS). MgB$_2$ powders used were also observed by SEM and a transmission electron microscope (TEM) to confirm its size, chemical composition and crystallography. A TEM (JEOL-4010T, JEOL. Co.) was operated at 400 kV, and qualitative data were also obtained from MgB$_2$ powders by electron energy loss spectroscopy (EELS) and EDS.

3. Results and Discussions

3.1 Microstructures

Figure 1(a) shows a SEM image of MgB$_2$ powders before grinding. Size distribution is very wide; smaller particles less than 5 $\mu$m can be seen, as can aggregate larger than 44 $\mu$m. As shown in Fig. 1(b), after grinding, particle size distribution was modified and particles smaller than 10 $\mu$m were frequently observed. A portion of grinded powders was placed on a carbon mesh supported Cu-grid and structure and chemical composition were confirmed by TEM. Figure 2(a) shows a bright field TEM image of a particle. The particle was dark and had facets. The selected area diffraction pattern (SADP) was obtained from this particle; it was indexed as a crystal lattice of AlB$_2$ structure, and its indices is described in Fig. 2. TEM image of a grinded particle. (a) bright field image of particle, (b) EELS and (c) EDS profiles obtained from the same particle as (a). A selected area diffraction pattern appearing in the inset of (a) was indexed as the AlB$_2$ structure.
an SADP shown in an insert of Fig. 2(a). The edge of 188 eV in the EELS profile of Fig. 2(b) detected from this particle corresponds to the B-K edge. A higher Mg-K peak in Fig. 2(c) was also obtained from this particle by EDS. The Cu-K peak of 8 keV is an artifact of the Cu-grid used. Figure 3(a) shows the macrostructure of the high $V_f$ sample. The billet of the high $V_f$ sample was cut along its vertical direction. The left and right sides correspond to the bottom and top sides of the steel mold, respectively. No remarkable shrinkages, cracks, large aggregations of powders or any other defects are observed. Gray and bright contrasts appear in this figure and correspond to a reinforced region and pure Al without particles, respectively. The region of Al was observed at the bottom side of the steel mold, indicating that the molten Al sufficiently penetrated to the bottom side through the preform of MgB$_2$ and could be turned back to the preform by the applied pressure. The region indicated by a rectangle in Fig. 3(a) was observed by SEM and its SEM image is shown in Fig. 3(b). Particles showed homogeneous distribution, and no cracks between particles and the Al matrix are observed at this magnification. Figure 3(c) shows an SEM image obtained from the low $V_f$ sample. In this case, MgB$_2$ particles underwent slight aggregation during fabrication of the composite material, because its fabricating method differed from that used for the high $V_f$ sample. Figure 4 shows the result obtained from the high $V_f$ sample by SEM-EDS observation. Comparing Figs. (a), (b) and (c), darker gray contrasts in the SEM image of (a) correspond to the brighter regions in the Mg-K map of (b), and this region almost corresponds to the black regions in Al-K map of (c). This means that reaction products consisting of MgB$_2$ and molten Al; for example, Mg-Al intermetallic compounds, MgO or AlB$_2$ were not formed in this sample.
3.2 Superconductivity

Figure 5 shows electrical resistivities (\(\rho\)) obtained from high \(V_f\), Low \(V_f\) and 99.99% purity Al (pure Al) samples. Composite materials show larger drops in \(\rho\) at about 40 K than does pure Al; the high \(V_f\) sample shows a drastic drop in \(\rho\). Figure 6(a) shows an enlarged view of \(\rho\) of the high \(V_f\) below 40 K. \(\rho\) decreased drastically at about 39 K (onset-\(T_c\)), became moderate at 37 K, and kept dropping to finally become \(\rho = 0\) at 22 K. Nagamatsu et al. reported a clear result of superconducting transition at 39 K. The discontinuity at 37 K in our sample is believed to be the effect of mixture with Al matrix, because our sample also shows a sharp drop in \(\rho\) at 39 K. Magnetization was also measured and it was showed in Fig. 6(b). Magnetization also shows a drastic drop at 37 K. From these results, \(T_c\) of the high \(V_f\) sample is 37 K. Figure 7 shows a picture of the high \(V_f\) sample floating above a permanent magnet in liquid He. This figure is not very clear, because liquid He boiled during the photography process. This means the high \(V_f\) sample shows the Meissner effect and has real superconductivity.

Magnetization of the high \(V_f\) sample at 5 K was measured for different applied magnetic fields. From Fig. 8(b), the lower critical field \((H_{c1})\) for the high \(V_f\) is about 0.5 kG, and from Fig. 8(a), the upper one \((H_{c2})\) is about 30 kG. The target \(V_f\) of the high \(V_f\) sample was 40%; however, a region without MgB\(_2\) particles was observed in the billet as shown in Fig. 3(a). The \(V_f\) for superconductivity was determined by the following equation: \(^{14}\)

\[
V_f = \frac{(\Delta M/\Delta B)}{-\frac{1}{1 - N} \times \frac{1}{4\pi}}
\]

where \(\Delta M/\Delta B\) is a slope of Fig. 8(b), which is an enlarged view of Fig. 8(a) at the lower side of applied fields, and is \(-0.0545\) emu/cm\(^3\) G. In the present work, the anti-magnetic coefficient, \(N\), which depends on the shape of samples, is assumed to be 0.25. The \(V_f\) for superconductivity of high \(V_f\) sample was estimated as approximately 50%. When the sample for measurement was cut from a billet, a region without MgB\(_2\) powder was removed. Consequently, net \(V_f\) of the high \(V_f\) sample increased in relative terms. For
convenience, the following equation\(^\text{15}\) was tentatively applied to estimate the critical current density \((J_c)\).

\[
J_c = \frac{20 \times \Delta M}{V \times (1 - \frac{t}{3 \times l})}
\]

(2)

where \(\Delta M\) is the rate of magnetization, \(V\) is the volume of the sample, \(t\) and \(l\) are thickness and length of the sample. The \(J_c\) was estimated about \(1.7 \times 10^4\) A/cm\(^2\) when \(\Delta M/V, t\) and \(l\) were 100 emu/cm\(^3\), \(5 \times 10^{-3}\) cm\(^3\), 1.0 mm and 2.0 mm, respectively. As this value, of course, means an apparent \(J_c\) because of discontinuous linkage of each MgB\(_2\) particle in the composite material. This is possibly the reason why it is lower than those generally reported; \(\sim 5 \times 10^5\) A/cm\(^2\).\(^{5,6}\)

### 3.3 Thermal property

Figure 9 shows thermal conductivities, \(\kappa\), obtained from the high \(V_f\), low \(V_f\), and pure Al samples. For example, comparing them at 10 K, both composite materials have \(\kappa\) values of at 30 and 7 W/K m lower than 2000 W/K m of pure Al. \(\kappa\) of low and high \(V_f\) samples are, however, higher than \(\sim 1\) W/K m of MgB\(_2\) compound reported by Schneider \textit{et al}.\(^{16}\) \(\kappa\) of commercial superconductors of NbTi and Nb\(_3\)Sn is about 0.5 W/K m; thermal conductivity of the composite materials in the present work is more than 10 times of this value. As shown in Fig. 9, when the temperature is assumed to be 30 K for a practical use of MgB\(_2\) superconductor, the low and high \(V_f\) samples show \(\kappa\) values of 70 and 25 W/K m, which are much higher than 0.5 W/K m of NbTi and Nb\(_3\)Sn.\(^{17,18}\) This thermal conductivity is important when the composite materials are to be formed into wires, because good thermal conductivity is expected to improve stability of the superconducting magnet, and avoids the quenching phenomenon.

Figure 10 shows specific heat determined for the composite materials. According to Debye’s model, specific heat at low temperature is described by the following equation,\(^{19}\) and the curvature of \(C/T - T^2\) becomes linear.

\[
C = \gamma T + \beta T^3
\]

(3)
In Fig. 10, the high $V_f$ sample shows a convex at 37.4 K. This result can be concluded as a jump in specific heat by the second transition with the energy gap in the superconductor,$^{19,20}$ and this is also important evidence on the thermal property of superconducting materials.

### 3.4 Extruded rod of high $V_f$ sample

Figure 11 shows an outline of the extruded high $V_f$ sample. A billet of half length ($\sim 20$ mm) was extruded together with a billet of pure Al having the same size, and a rod of 10 mm diameter and 85 mm length was obtained in the present work. The left and right side of Fig. 11(a) correspond to the end and top of the extruded rod. Figure 11(b) shows a macrostructure of this rod cut along the longitudinal direction of the rod. The top of rod (region A) is obviously pure Al, and region B, which measures 10 mm in diameter and 50 mm in length, is obviously the composite. Region A includes some cracks, and is omitted for measurement of $T_C$. Figure 12 shows SEM images obtained from the extruded high $V_f$ sample. SEM images were obtained from directions parallel to and perpendicular to the direction of extrusion (E.D.), and show microstructures similar to that shown in Fig. 3(b) and no remarkable defects. Figure 13 shows changes in electrical resistivity with temperature. The extruded sample and the billet sample mostly show similar behavior for drop in resistivity with decreasing temperature, and onset $T_C$ of the extruded sample is about 39 K. Note that drop in resistivity below $T_C$ of the extruded sample is more drastic than that of the billet sample. Magnetization of the extruded sample for different applied field was measured in the same way as for the billet sample. $H_{C1}$ and $H_{C2}$ are about 500 and 70000 G, respectively. $\Delta M/\Delta B$ was $0.0866$ emu/cm$^3$ G and $V_f$ for superconductivity of this sample was estimated from eq. (1). $J_c$ of the extruded sample was also estimated by the eq. (2), it is about $1.3 \times 10^6$ A/cm$^2$, and this is similar to a billet of the high $V_f$ sample. $V_f$ for superconductivity is about 82%, which explains why the onset $T_C$ is more obvious than that of the billet sample. $V_f$ of the sample has probably been changed by extrusion, because Al matrix flows easier than MgB$_2$ particles during hot-extrusion.

### 4. Conclusions

Billet and extruded rods of composite materials consisting of MgB$_2$ dispersed in aluminum matrix were fabricated, and were confirmed to exhibit superconductivity.
(1) MgB$_2$-dispersed aluminum matrix composite materials that include high and low volume fractions of MgB$_2$ powders were successfully fabricated. No remarkable defects were observed in these composite materials. SEM-EDS did not detect any reaction products such as Mg-Al, or Mg oxides.

(2) The high V$_f$ sample showed an onset $T_C$ of electrical resistivity of 39 K. Magnetization of this sample also decreased at 39 K. From the result of magnetization, volume fraction for superconductivity and critical current density of this high V$_f$ sample were estimated as 50% and $1.7 \times 10^4$ A/cm$^2$.

(3) The high V$_f$ sample was confirmed to exhibit the Meissner effect by floating above a permanent magnet in liquid He.

(4) The thermal conductivity of the high V$_f$ sample at 10 K was higher than that of MgB$_2$ compound.

(5) Temperature dependence of the specific heat was measured for the high V$_f$ sample and its curve shows a convex at 37.4 K. This indicates a jump of specific heat by the second transition with the energy gap in the superconductor.

(6) The high V$_f$ sample was hot-extruded into a 10 mm$\phi$ rod, and no remarkable defects were observed. This extruded sample also showed onset $T_C$ of electrical resistivity of $\sim$39 K, as did a billet of the high V$_f$ sample, and drop in electrical resistivity at 39 K was more drastic than that of the billet sample. V$_f$ for superconductivity was estimated as 82%, and critical current density of this high V$_f$ sample was estimated as $1.3 \times 10^4$ A/cm$^2$.

Acknowledgement

This project was supported by 2002–2004 research projects in Venture Business Laboratory of Toyama University, Japan.

REFERENCES

10) http://teleradiology.jp/MRI/12_MRI/MRLjiko/