論文内容の要旨

論文題目 Electrical and Mechanical Properties of MgB_2 Wires Fabricated by an Internal Mg Diffusion Process
（Mg の内部拡散法によって製作した MgB_2 線材の電気的および機械的性質）

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Ⅰ. INTRODUCTION

A common fabrication method for MgB_2 wire or tape is the Powder in Tube (PIT) process. This conventional process is based on the powder metallurgy (PM) accompanying densification and shrinkage after sintering. Giunchi *et al* made an adventurous attempt with a process that reported a successful result for MgB_2 superconductor wire [1]. In this process, a composite billet composed of a steel pipe internally lined with Nb tube is filled with a coaxial internal pure Mg rod and B powder. However, their J_c values are not so high at 4.2 K and large magnetic fields probably due to the high heat treatment temperature of 850-900 ^{o}C which decreases the upper critical field [2]. Very recently, they also tried C-doping to the wire and obtained the increase of B_{irr} from 10 to 16 T at 4.2 K [3]. Togano *et al* fabricated MgB_2/Fe wires with a similar method using Mg-Li alloy tube or rod, which is more easily mechanically cold worked than pure Mg [4-5]. It showed that the reacted MgB_2 layer has dense structure. However, the Li was diffused into MgB_2 layer and J_c values of MgB_2 layer showed a decrease as a result.

In this research, critical current density using a classical diffusion process without any pressure was achieved as much as that of Nb_3Sn. One of the remarkable properties of an internal Mg diffusion process (IMD) is quite hard dense structure. Heat treatment temperature dependences of critical current (I_c), cross sectional area of the reacted layer, critical current density (J_c) and Vickers hardness with each different sheath of Fe and Ta were systematically investigated. The fabrication and characterization of MgB_2 wire, both monocore and multicore, with non-doped and 10 mol% SiC doped samples were also carried out.

Ⅱ. FABRICATION OF WIRES

The process of this research is basically the same as that reported by Togano *et al* [4]. The schematic of the IMD processed multicore wire is shown in figure 1. The prepared sheath material is pure Fe or Ta tube with an outer diameter of 6 mm, an inner diameter of 4 mm and a length of 50 mm. A pure Mg rod with a diameter of 2 mm was placed at the center of Fe or Ta tube, and the empty space between the Mg rod and the Fe or Ta tube was filled with the amorphous B powder (99.99%, -300 Mesh) or the powder mixture of B and 5 or 10 mol% SiC (a few tenths nanometer size) as shown in figure 1. The weight ratio of Mg rod to packed powders was about 3:1 (for B+5 or 10 mol% SiC mixed powder). The Mg rod is prepared extra amount in order to compensate the loss by oxidation and evaporation above the Mg melting point (650 ^{o}C). In monocore case, the composite performed initially swaging until a rod shape with an outer diameter of 4 mm and then wedged the rod into the Cu-20wt%Ni sheath with an inner diameter of 4 mm and an outer diameter of 6 mm. The prepared sample was groove-rolled into a rod shape with 2.3 x 2.3 mm^2 cross section and then drawn into a wire of 1.3 mm in diameter.

In multicore case, seven pieces of the 7 monocore wires of 1.3 mm diameter and 47 mm length of Fe or Ta were bundled and inserted into the 4 mm hole of the Cu-20%Ni tube of 6 mm outer diameter. Then the composite was cold worked into a wire of 1.3 mm outer diameter by the same process for the monocore wire. The samples cut at a length of 40 mm were heat treated between 600 and 800 ^{o}C from 0.25 to 10 hr under Ar gas atmosphere. During heat treatment, the samples were wrapped with a zirconium foil in order to minimize oxidation.

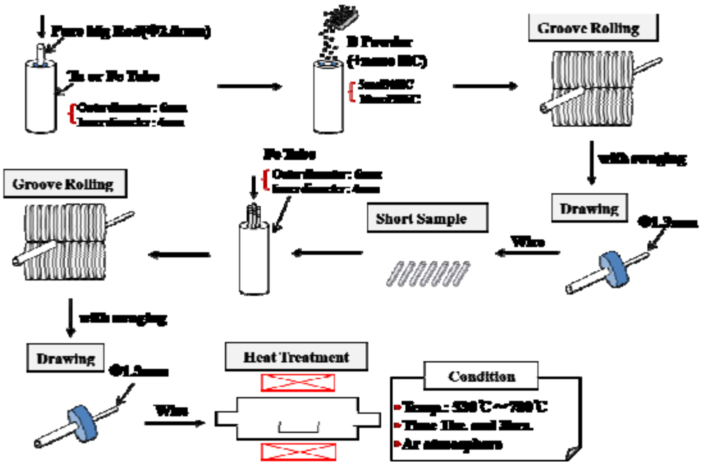

Figure 1 Schematic illustration of the multicore wire fabrication process

Ⅲ. RESULTS AND DISCUSSION

A. Microstructure for monocore and multicore

Figure 2 (a) and (b) shows optical micrographs of the polished transverse and longitudinal cross sectional area of the Ta sheathed 10 mol% SiC doped multicore after cold working. The composite of the pure Mg/[B(-SiC) powder]/Ta/Cu-20wt%Ni tube with an outer diameter of 6 mm was successfully cold worked into a 1.3 mm wire at room temperature without any breakage of Mg in spirit of very poor workability of pure Mg. It supposes that workability of pure Mg is overcame without any breakage by IMD process because of confinement by boron powder with Ta or Fe sheath of good workability.

Figure 2 (c) and (d) shows transverse and longitudinal cross sectional area of this multicore wire heat treated at 645 ^{o}C for 1hr, respectively. Figure 2 (e) and (f) shows transverse cross sectional area of Fe and Ta sheathed 10 mol% SiC doped monocore wire heat treated at 640 ^{o}C for 1 hr. Although remarkable shrinkage for both monocore and multicore wire occurred after sintering, the diffused MgB_2 layer showed uniform deformation without porosity inside the microstructure. During the heat treatment, liquid Mg seems to infiltrate into the boron layer to form MgB_2 layer along the inner wall of the Fe or Ta sheath, which is seen as a ring on the cross section. As the structure is the same even when the heat treatment temperature is below the Mg melting point, Mg may be melted by heat generated by the exothermic reaction forming MgB_2 at the B/Mg interface.

Figure 3 shows the SEM image of reacted MgB_2 layer compared with that of PIT processed wire. The PIT-processed wire shows granular MgB_2 microstructure, which is typical for PIT processed MgB_2. On the other hand, IMD processed wire shows much denser structure than that of the PIT processed wire, and there is not porosity. It depends on the volume faction of raw boron powder. Being isolated from Mg, denser packed boron powder in IMD process caused denser MgB_2 structure. In conventional *in-situ* PIT process, boron powder mixed with Mg forms porous microstructure of low density. The amount of remaining Mg decreases with the increasing in the heat treatment temperature and dwell time. However, we need to take into account of the evaporation and/or leakage of Mg. Such evaporation and/or leakage of Mg are suppressed for longer wires, and higher J_c can be expected.

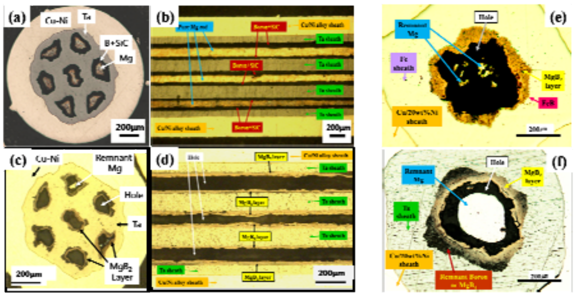

Figure 2 Optical micrographs polished (a), (c) transverse (b), (d) longitudinal cross sectional area of Ta sheathed 10 mol% SiC doped multicore wire (a), (b) after cold working and (c), (d) after heat treatment at 645 °C for 1 hr. Transverse cross sectional area of (e) Fe , (f) Ta sheathed 10 mol% SiC doped monocore wire heat treated at 640 °C for 1 hr.

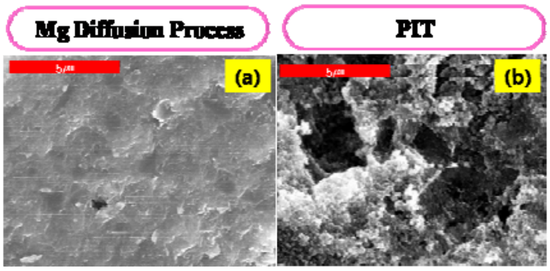

Figure 3 SEM image of microstructure of (a) IMD processed wire and (b) PIT processed wire.

B. Fe or Ta sheathed monocore

The heat treatment temperature dependence of transport critical current (I_c), cross sectional area of the reacted layer, critical current density (J_c), and Vickers hardness (HV) for dwell time of 0.5 hr are shown in figure 4. The I_c, and J_c of 10 mol% SiC doped samples are higher than those of non-doped samples. It is well known H_{c2} enhancement caused by the fact that the C atoms from the SiC powder can effectively substitute on the B site [6]. Also, the maximum values of I_c and J_c for non-doped and 10 mol% SiC doped samples occur at a heat treatment temperature of 640 °C. The origin of the maximum is considered to be a competition between J_c increase by the progress of MgB_2 forming reaction and J_c decrease by the MgB_2 grain growth with increasing heat treatment temperature. The I_c for monocore in Ta sheath is almost the same or slightly lower than Fe sheathed monocore samples. Kovac *et al*. reported that the higher MgB_2 core density corresponds to the stronger metallic sheath [7]. So, excellent J_c is obtained from Ta sheathed monocore, considering that HV of Ta sheath (~HV 204) is stronger than that of Fe sheath (~HV 118). In fact, a comparison of density relative to HV in Ta and Fe sheath is difficult because of improved grain connectivity, nano-sized MgB_2 grain, solid solution strengthening by decomposed C and Si. The other reasons of hardening expect to the hardening by SiC or processing are taken account into the age hardening or affection of secondary phase such as MgO.

In the previous work of Husek *et al*., they reported a good correlation between density and measured HV [8]. The superior value of HV of typical MgB_2 wire by an *ex-situ* PIT process was about HV 400 due to the numerous pores and the microstructure. HV 1700, the highest hardness in MgB_2 bulk, was achieved with the hot isotropic press (HIP) method by Takano *et al* [9]. As shown in figure 4, the highest value of HV for our samples reaches 1700, which is 4 times higher than that for conventional PIT-processed wire and is almost the same as that of bulk sample. From the above comparison, it is found that wires fabricated by this IMD process bring quite high density, which should be the origin of the high J_c.

As a result, for Ta sheathed 10 mol% SiC doped monocore sample heat treated at 640 °C for 0.5 hr, J_c at 4.2 K and 7 T reached the value of 300k A/cm^2, which is 3 times higher than that of recently reported conventional *in-situ* PIT processed wires.

C. Ta/Cu-20wt%Ni sheathed monocore and multicore

The critical current density (J_c) for 10 mol% SiC doped monocore and 7 multicore wires with Ta sheath inserted into the Cu-20wt%Ni sheath show similar trends for heat treatment temperature at the dwell time of 1 hr as shown in figure 5. Although the area of the reacted layer in monocore increases with increasing temperature, the area in multicore is almost constant. This means that the reaction between B and Mg to form MgB_2 is finished at even the lowest heat treatment temperature of 600 °C for 1 hr in the multicore sample, because of sufficiently shorter diffusion length. As a result, I_c for the multicore is higher than that for the monocore. The larger I_c is important especially for the practical use.

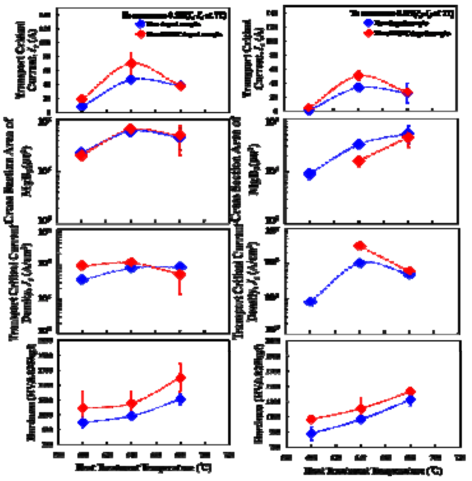

Figure 4 I_c, cross sectional area, J_c at 7 T and 12 T and Vickers hardness of IMD-processed wire heat treated at 600 °C, 640 °C and 680 °C for 0.5 hr ; black (non-doped) and red (10 mol% SiC doped).

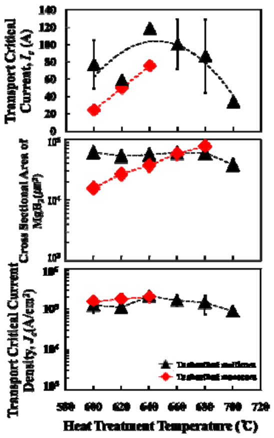

Figure 5 Averaged I_c, cross sectional area and averaged J_c at 7 T and 4.2 K for Ta sheathed 10 mol% SiC doped multicore and monocore wires heat treated at various temperature for 1 hr; black closed triangle (multicore) and red closed diamond (monocore).

Ⅳ. CONCLUSION

In this thesis, it was found that the internal Mg diffusion (IMD) process achieved much improved MgB_2 core density and, hence, much enhanced critical current density (J_c) values. The highest J_c value was obtained for Ta sheathed 10 mol% SiC doped 7 multicore wires and was exceedingly over 300k A/cm^2 at 7 T in 4.2 K and about over 3 times higher than those of *in-situ* powder in tube (PIT) processed wires (about 90k A/cm^2) and was reached to almost practical level of J_c values as shown in figure 6.

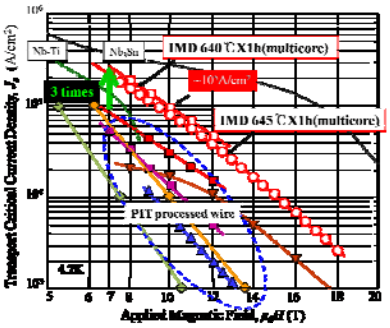

Figure 6 Applied magnetic field dependence of transport J_c for reported highest J_c values of IMD processed Ta/Cu-20wt%Ni sheathed 10 mol% SiC doped MgB_2 wire compared with applied highest J_c values of conventional PIT processed wire, Nb-Ti and Nb_3Sn superconductor wire or tape.

Reference

[1] Giunchi *et al* 2003 *Supercond. Sci Technol.* **16** 285-291

[2] Kumakura *et al* 2005 *Supercond. Sci. Technol*. **18** 1042-46

[3] Giunchi *et al* 2007 *IEEE Trans. Appl. Supercond*. **17** 2761-65

[4] Togano *et al* H 2007 *Supercond. Sci. Technol*. **20** 629-633

[5] Togano *et al* 2007 *Supercond.Sci. Technol*. **20** 239-243

[6] Sumption *et al* 2004 *Supercond. Sci. Technol.* **17** 1180

[7] Kovac *et al* 2008 *Supercond. Sci. Technol.*21 015004

[8] Husek *et al* 2004 *Supercond. Sci. Technol.***17** 971

[9] Takano *et al* 2001 *Appl. Phys. Lett*. **78**, 2914