Journal of the Korea Institute of Applied Superconductivity and Cryogenics
Vol.5, No.3, (2003), pp.6~10

Influence of Ag nano-powder additions on the superconducting properties of MgB_2 materials

K. J. Song, S. J. Choi, S. W. Kim, C. Park, J. H. Joo, H. J. Kim,
J. K. Chung, R. K. Ko, H. S. Ha, E. Y. Lee, G. H. Rim, and Y. K. Kwon
Korea Electrotechnology Research Institute, Changwon, 641-120 Korea

kjsong@keri.re.kr

***Abstract* – Silver nano-powder was added to MaB_2 to make $(Ag)_{(x)wt.\%}(MgB_2)_{(100-x)wt.\%}$ (Ag_x-MgB_2) ($10 \leq x \leq 50$) composite superconductors to investigate the effect of the Ag nano-powder on the vortex pinning. Pellets made out of the mixed powder were put inside stainless steel tubes, which were sintered at 850° C in Ar atmosphere. No impurity phase was identified for as-rolled samples. However, both the MgB_2 and the Ag_x-MgB_2 composite pellets, when sintered, contain small amount of MgB_4 and MgAg impurity phases. From the magnetization study, it was found that the flux pinning was improved in the high magnetic field region (> 3 T) only when 10w/o Ag was added to MgB_2. The "two step" structures in ZFC $M(T)$ curve gradually increased as the amount of Ag added increased. Pinning centers can be created by adding a suitable amount of Ag nano-powder which is not too large to increase the decoupling between the MgB_2 grains.**

Keywords : MgB_2 powder, Ag nano-powder, sintering or as-rolled, critical currents, vortex pinning, magnetization.

1. INTRODUCTION

The binary intermetallic magnesium diboride (MgB_2), which was discovered to be superconducting at temperature below ~39 K, in 2001 [1], has attracted much attention in both fundamental properties and practical applications.

The new MgB_2 superconductor has exhibited a variety of interesting physical phenomena, including the property of conventional BCS theory [2]-[3]; strong-link current flows between grains [4] and stability of supercurrents with time [5], in contrast to weak-link problems and giant flux creep found in high-T_c cuprate superconductors; the anisotropy of its upper critical magnetic field H_{c2} [6]-[9]; and two superconducting gaps in MgB_2 [10]-[13].

Meanwhile, this new superconductor is known to have many features suitable for superconducting wires/tapes because of the rapid and reliable compound synthesis, relative simplicity in both structure and components, the commercial availability of MgB_2 powder, etc. Unfortunately, the applications of these wires/tapes might be limited because of both the low-lying irreversibility line $H_{irr}(T)$ and the rapid degradation of current carrying capability under magnetic field. The low cost and the simplicity of the fabrication of wires/tapes out of the MgB_2, however, are motivating the effort to utilize this new superconductor. At the beginning, Jin et al. [14] showed the fabrication of dense and metal-clad MgB_2 superconductor wire with a transport J_c greater than 36,000 A/cm^2 at 4.2K. Many research groups [15]-[20] reported the fabrication of MgB_2 wires/tapes, as well. Recently, it has been reported that prototype MgB_2 wires/tapes in lengths with superconducting properties good enough to be used for practical applications was developed [21].

Transport J_c can be improved by optimizing the processing conditions, and that in the presence of magnetic field can be enhanced further by reducing flux creep by introducing pinning centers. Processing high temperature superconductors with Ag which is chemically compatible is common in the fabrication of high-T_c tapes/wires (PIT BSCCO tapes). Similarly, fine Ag particles, when uniformly distributed in the MgB_2 matrix, can play the role of pinning centers and at the same time improve the connectivity of MgB_2 grains in the Ag-MgB_2 wires/tapes.

In this paper, a series of Ag-MgB_2 composite superconductors, containing different amount of Ag nano-powder have been prepared, and the effect of the adding Ag nano-powder on the superconducting properties was investigated.

2. EXPERIMENTAL ASPECTS

A series of Ag_x-MgB_2 composite superconductors were prepared by adding Ag nano-powder (~100 nm size) to MgB_2 using a simple solid-state reaction route. The mixed powder was ball-milled for 10 hours. The $(Ag)_{(x)wt.\%}(MgB_2)_{(100-x)wt.\%}$ (Ag_x-MgB_2) ($10 \leq x \leq 50$) pellets were made with ~ 600 kg/cm^2 uniaxial pressure at room temperature. The pellets were put in a stainless steel tube, which was sealed by a stainless steel cap with screw. A small amount of MgB_2 powder was put inside the tube to reduce the loss of Mg. The pellets in the tube were sintered at 850° C for 4 hours in Ar atmosphere.

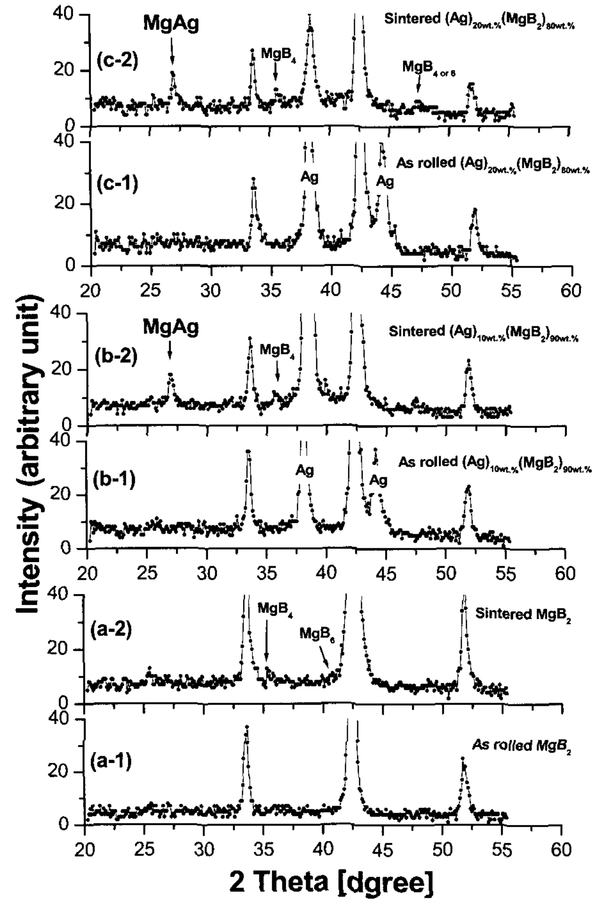

Fig. 1. The typical diffraction patterns for the both sintered and as-rolled (a) MgB_2, (b) $(Ag)_{10wt.\%}(MgB_2)_{90wt.\%}$ and (c) $(Ag)_{20wt.\%}(MgB_2)_{80wt.\%}$ pellet samples

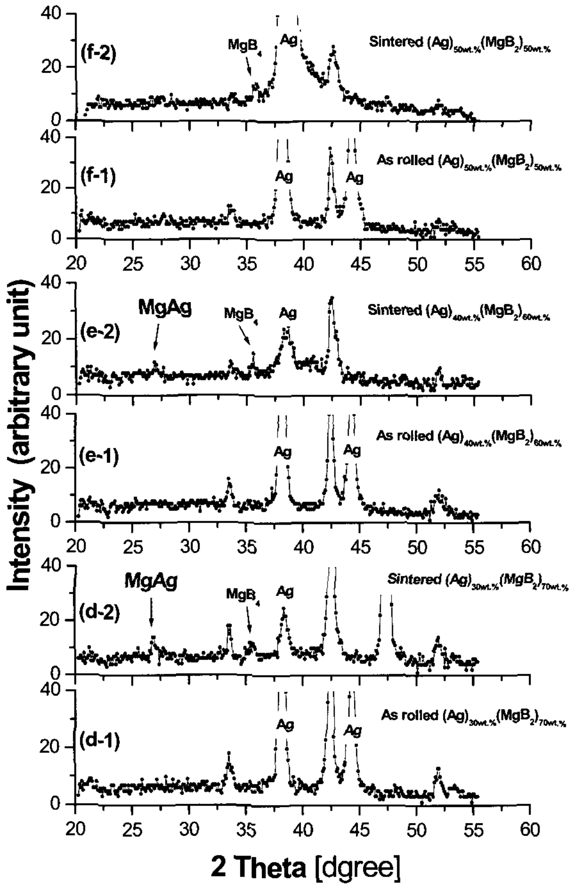

Fig. 2. The typical diffraction patterns for the both sintered and as-rolled (d) $(Ag)_{30wt.\%}(MgB_2)_{70wt.\%}$, (e) $(Ag)_{40wt.\%}(MgB_2)_{60wt.\%}$ and (f) $(Ag)_{50wt.\%}(MgB_2)_{50wt.\%}$ pellet samples.

Characterization methods included both X-ray diffraction and studies of magnetization *M*. X-ray diffraction was used to investigate the phases evolved during sintering. The magnetization studies for both the sintered and the as-rolled Ag_x-MgB_2 composite superconductors were conducted using commercial

PPMS-9T (USA Quantum Design Cop.). The isothermal magnetizations *M*(*H*) of the series of samples were measured at temperatures between 5 to 50 K in fields up to 5 *T*. *The critical current density* (J_c) *values have been* obtained from the *M*(*H*) data, using Bean model, for the Ag_x-MgB_2 composite superconductors.

3. RESULTS AND DISCUSSIONS

Ag nano-powder was added to the MgB_2 powder to introduce pinning centers in the Ag_x-MgB_2 composite superconductors. Dense and hard MgB_2 or Ag_x-MgB_2 pellet samples were made through sintering at 850° C for 4 hours in Ar atmosphere. The sealing of the stainless steel tube was not complete, but there was no loss of Mg, which was confirmed by comparing the masses before and after the high temperature sintering. Pinning centers can be introduced in MgB_2 or Ag_x-MgB_2 composite superconductors by sintering. As more Ag is added, the samples with more silver added were denser than those with less amount of Ag added.

The phases present in both sintered and as-rolled MgB_2 and Ag_x-MgB_2 were investigated using XRD θ-2θ scans which are shown in Fig. 1 and 2. No impurity phase was identified, and all the peaks could be indexed as MgB_2 or Ag, for all the as-rolled samples. However, both the MgB_2 and the Ag_x-MgB_2 pellets, sintered at 850°C for 4 hour in argon, contain small amount of MgB_4 or MgAg impurity phases. As shown in Fig. 1 and 2, a peak from MgAg appeared in the XRD pattern of the sintered MgB_2 with 10 to 40w/o Ag added. The amount of MgAg phase decreases as more Ag nano-powder is added.

For magnetization study, the pellets were cut into pieces with the size of ~3mm x 3mm x 3 mm. The superconductive magnetizations for both the sintered and the as-rolled pellet samples were investigated using PPMS. The isothermal magnetization *M*(*H*) was measured at temperatures between 5 and 50 K in magnetic fields up to 5 T. Values of magnetization (*M*) were corrected for the background *M*, measured at temperatures above T_c. Below T_c and below the irreversibility line H_{irr}, the magnetization was hysteretic due to the presence of intragranular persistent currents.

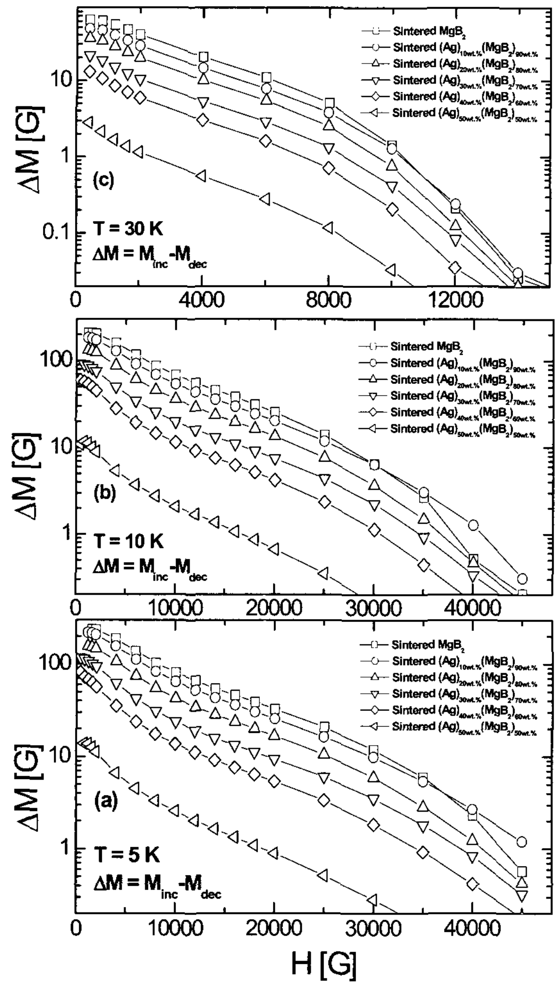

Fig. 3. The magnetic irreversibility ΔM versus magnetic field (H) for the sintered both MgB_2 and Ag-MgB_2 samples (from 10 wt.-% to 50 wt.-%) at (a) $T = 5$ K, (b) $T = 10$ K and (c) $T = 30$ K.

From the magnetic irreversibility $\Delta M = [M(H_{dec}) - M(H_{inc})]$, which is the difference of magnetization M between the increasing field and the decreasing field branches, in units of [emu cm^{-3}] = [G], the persistence current density was obtained using the Bean critical state model [22], $J \propto 15\Delta M/r$, where r is the mean grain radius.

Fig. 3 shows the magnetic irreversibility ΔM versus magnetic field (H) for both sintered MgB_2 and sintered Ag_x-MgB_2 at (a) T = 5 K, (b) T = 10 K and (c) T = 30 K. As shown in Fig. 3, the magnetic irreversibility ΔM*'s* (that are proportional to persistence current density) of the Ag_{50}-MgB_2 are much lower than both sintered MgB_2 and Ag_{10}-MgB_2. Fig. 3 shows that the amount of Ag nano-powder in Ag_x-MgB_2 leads to differences in irreversibility magnetizations that are directly related to J_c values. The amount of Ag to fill the pores and to form a thin layer of Ag at the boundary between MgB_2 particles (grains) just enough not to disturb the inter-particle (inter-grain) current flow is what is needed to enhance the superconducting properties by improving the connectivity between the particles. The optimum amount of Ag to be added to MgB_2 lies below 10 w/o because ΔM*'s* decrease as more Ag than 10w/o is added as shown in Fig. 3. Several research groups [23]-[26] reported the enhancement of the flux pinning in bulk MgB_2 was made by adding nano-particles. The results in Fig. 3 show that the flux pinning was improved in the high magnetic field region only when 10w/o Ag was added to MgB_2.

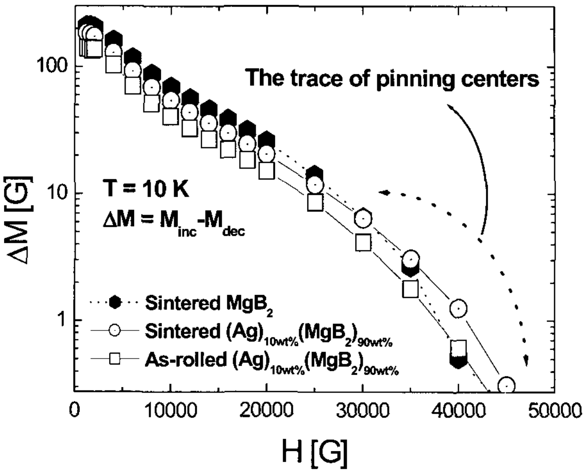

Fig. 4. The magnetic irreversibility ΔM versus magnetic field (H) for the sintered both MgB_2 and $(Ag)_{10wt.\%}(MgB_2)_{90wt.\%}$ samples at $T = 10$ K

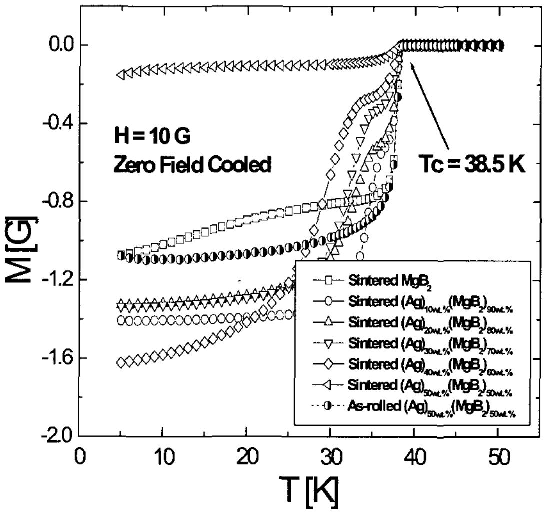

Fig. 5. Zero Field Cooled magnetization M versus temperature T in an applied field H = 10 G for the sintered both MgB_2 and Ag-MgB_2 composite superconductors (10 to 50 wt.-% Ag nano-powder additions) and as-rolled $(Ag)_{50wt.\%}(MgB_2)_{50wt.\%}$ composite superconductor.

Fig. 4 shows the magnetic irreversibility ΔM versus magnetic field (H) at $T = 10$ K for both the MgB_2 and the Ag_{10}-MgB_2. There are traces of pinning centers created by 10w/o Ag nano-powder additions at the high magnetic field region (above ~ 3 T) in both the as-rolled and the sintered ones. As mentioned in Fig. 1 and 2, impurity phases such as MgB_4, MgB_6 and MgAg, are formed in Ag_x-MgB_2 when sintered. These impurities can play a role as pinning centers in Ag_x-MgB_2 composite superconductors. The ΔM of MgB_2 falls off more rapidly than that of Ag_{10}-MgB_2 when the field is higher than ~3 Tesla. Pinning centers can be created by adding a suitable amount of Ag nano-powders to MgB_2, which can also help improve the connectivity between the grains. This effect will be further enhanced if the Ag nano-particles are distributed uniformly.

It has been reported that the pores became smaller and less irregular in shape and the mechanical property was improved when Ag was added to YBCO through solution, which resulted in uniform distribution of fine Ag particles in YBCO [27]-[28]. If optimum amount of Ag nano-particles can be uniformly introduced in MgB_2 like that in YBCO, enhanced flux pinning in MgB_2 can be expected. The understanding of the mechanism for creating pinning centers using Ag nano-powder in MgB_2 is needed to realize this.

In general, the superconductive transition temperature T_c is determined by linearly extrapolating to zero in Field Cooled (FC) magnetization $M(T)$ or in Zero Field Cooled (ZFC) magnetization $M(T)$ curves. This procedure ignores the slight tail at high temperature resulting from the thermal fluctuation effects. Fig. 5 shows that T_c is about 38.5 K for all pellet samples. While the ZFC transition of the as-rolled Ag_{50}-MgB_2 changes smoothly with temperature, the Meissner state magnetic moment under ZFC condition in an applied field 10 G (magnetization $M(T)$ curves) for the sintered Ag_x-MgB_2 have more structures as seen in Fig. 5. These "two step" transition is from the decoupling of current flow between grains [29]. It is evident from Fig. 5 that the structure gradually increases as the amount of Ag nano-powder added increases. This means that the increase of the amount of Ag nano-powder added to MgB_2 diminishes the supercurrent flow between grains and weakens the inter-grain coupling.

4. SUMMARY

Silver nano-powder was added to MaB_2 to make $(Ag)_{(x)wt.\%}(MgB_2)_{(100-x)wt.\%}$ (Ag_x-MgB_2) ($10 \leq x \leq 50$) composite superconductors to investigate the effect of the Ag nano-powder on the vortex pinning. Pellets made out of the mixed powder were put inside stainless steel tubes, which were sintered at 850° C in Ar atmosphere. No impurity phase was identified for as-rolled samples. However, both the MgB_2 and the Ag_x-MgB_2 composite pellets, when sintered, contain small amount of MgB_4 and MgAg impurity phases. The amount of MgAg phase observed in sintered MgB_2 with 10 to 40w/o Ag added decreased as more Ag nano-powder was added. From the magnetization study, it was found that the flux pinning was improved in the high magnetic field region (> 3 T) only when 10w/o Ag was added to MgB_2. The structures in ZFC $M(T)$ curve gradually increased as the amount of Ag nano-powder added increased. The increase of the amount of Ag nano-powder added to MgB_2 more than 10w/o can diminish the supercurrent flow between grains and weaken the inter-grain coupling. Pinning centers can be created by adding a suitable amount of Ag nano-powders which is not too large to increase the decoupling between the MgB2 grains.

ACKNOWLEDGMENT

Authors wish to acknowledge fruitful discussions with Prof. J. H. Joo. This research was supported by grants from both Basic Research Program of KERI and Center for Applied Superconductivity Technology of the 21st Century Frontier R&D Program funded by the Ministry of Science and Technology, Republic of Korea.

REFERENCES

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, *Nature*, **401**, 63 (2001).

[2] D. K. Finnemore, J. E. Ostenson, S. L. Bud'ko, G. Lapertot, and P. C. Camfield, *Phys. Rev. Lett.*, **86**, 2420 (2001).

[3] S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, *Phys. Rev. Lett.*, **86**, 1877 (2001).

[4] D. C. Labalestier, M. O. Cooley, A. A. Polyanskii, J. Y. Jiang, S. Patnaik, X. Y. Cai, D. M. Feldmann, A. Gurevich, A. A. Squitieri, M. T. Naus, C. B. Eom, E. E. Hellstrom, R. J. Cava, K. A. Regan, N. Rogado, M. A. Hayward, T. He, J. S. Slusky, P. Khalifah, K. Inumaru, and M. Haas, *Nature*, **410**, 186 (2001).

[5] J. R. Thompson, M. Paranthaman, D. K. Christen, K. D. Sorge, H. J. Kim, and J. G. Ossandon, *Supercond. Sci. & Technol.*, **14**, L19 (2001).

[6] S. L. Bud'ko, V. G. Kogan, and P. C. Canfield, *Phys. Rev.*, **B64**, 180506 (2001).

[7] S. L. Bud'ko and P. C. Canfield, *Phys. Rev.*, **B65**, 212501 (2002).

[8] M. Angst, R. Puzniak, A. Wisniewski, J. Jun, S. M. Kazakov, J. Karpinski, J. Moos, and H. Keller, *Phys. Rev. Lett.*, **88**, 167004 (2002).

[9] U. Welp, A. Rydh, G. Karapetrov, W. K. Kwok, G. W. Crabtree, Ch. Marcenat, L. Paulius, T. Klein, J. Marcus, K. H. P. Kim, C. U. Jung, H. -S. Lee, B. Kang, and S. -I. Lee, *Phys. Rev.*, **B67**, 012505 (2003).

[10] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, S. G. Louie, *Nature*, **418**, 758 (2002).

[11] H. Schmidt, J. F. Zasadzinski, K. E. Gray, and D. G. Hinks, *Phys. Rev. Lett.*, **88**, 127002 (2002).

[12] M. Iavarone, G. Karapetrov, A. E. Koshelev, W. K. Kwok, G. W. Crabtree, D. G. Hinks, W. N. Kang, Eun-Mi Choi, Hyun Jung Kim, Hyeong-Jin Kim, and S. I. Lee, *Phys. Rev. Lett.*, **89**, 187002 (2002).

[13] M. R. Eskildsen, M. Kugler, S. Tanaka, J. Jun, S. M. Kazakov, J. Karpinski, and O. Fischer, *Phys. Rev. Lett.*, **89**, 187003 (2002).

[14] S. Jin, H. Mavoori, C. Bower, and R. B. van Dover, *Nature*, **411**, 563 (2001).

[15] G. Grasso, A. Malagoli, C. Ferdeghini, S. Roncallo, V. Braccini, A. S. Siti, and M. R. Cimberle, *Appl. Phys. Lett.*, **79**, 230 (2001).

[16] S. Soltanian, X. L. Wang, I. Kusevic, E. Babic, A. H. Li, M. J. Qin, J. Horvat, H. K. Liu, E. W. Collings, E. Lee, M. D. Sumption, and S. X. Dou, *Physica C*, **361**, 84 (2001).

[17] H. Kumakura, A. Matsumoto, H. Fujii, and K. Togano, *Appl. Phys. Lett.*, **79**, 2435 (2001).

[18] C. Buzea and T. Yamashita, *Supercond. Sci. & Technol.*, **14**, R115 *(2001)*.

[19] K. J. Song, N. J. Lee, H. M. Jang, H. S. Ha, D. W. Ha, S. S. Oh, M. H. Sohn, R. K. Ko, C. Park, Y. K. Kwon, and K. S. Ryu, *Physica C*, **370**, 21 (2002).

[20] K. J. Song, C. Park, N. J. Lee, H. M. Jang, H. S. Ha, D. W. Ha, S. S. Oh, M. H. Sohn, R. K. Ko, Y. K. Kwon, and J. H. Joo, *IEEE Trans. Appl. Supercond.*, **13**, 3221 (2003).

[21] Superconductor News (InfoClue Co., Ltd, 2003. 5. 23) reported 100m long MgB_2 is developed by JR Tokai and Hitachi Co., and Hyper Tech Research Inc. (Ohio, USA) has showed the MgB_2 coil at 2003 EUCAS Sorrento meeting.

[22] C. P. Bean, *Phys. Rev. Lett.*, **8**, 250 (1962), and *Rev. Mod. Phys.*, **36**, 31 (1964)

[23] J. Wang, Y. Bugoslavsky, A. Berenov, L. Cowey, A. D. Caplin, L. F. Cohen, J. L. MacManus Driscoll, L. D. Cooley, X. Song, and D. C. Larbalestier, *Appl. Phys. Lett.*, **81**, 2026 (2002)

[24] S. X. Dou, S. Soltanian, J. Horvat, X. L. Wang, S. H. Zhou, M. Lonescu, H. K. Liu, P. Munroe, and M. Tomsic, *Appl. Phys. Lett.*, **81**, 3419 (2002)

[25] D. Kumar, S. J. Pennycook, J Narayan, H Wang, and A. Tiwari, *Supercond. Sci. & Technol.*, **16**, 455 (2003)

[26] Qiang Li, G. D. Gu, and Y Zhu, *Appl. Phys. Lett.*, **82**, 2103 (2003)

[27] J. Joo, J-G. Kim, and W. Nah, *Supercond. Sci. & Technol.*, **11**, 645 (1998)

[28] J. Joo, S-B. Jung, W. Nah, J-Y. Kim, and T. S. Kim, *Cryogenics*, **39**, 107 (1999)

[29] J. R. Thompson, D. K. Christen, H. R. Kerchner, L. A. Boatner, B. C. Sales, B. C. Chakoumakos, H. Hsu, J. Brynestad, D. M. Kroeger, J. W. Williams, Yang Ren Sun, Y. C. Kim, J. G. Ossandon, A. P. Malozemoff, L. Civale, A. D. Marwick, J. K. Worthington, L. Krusin-Elbaum, and F. Holtzberg in "Magnetic Susceptibility of Superconductors and Other Spin Systems", edited by R. A. Hein, T. Francavilla, and D. Liebenburg, 157 (Plenum, New York, 1992).