Pinning enhancement in M/MgB$_2$ (M=Ag, Cu and Nb) system

Y. Kimishima, S. Takami, M. Uehara, T. Okuda and T. Kuramoto

Department of Physics, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

E-mail: kimi@ynu.ac.jp

Abstract. $J_c$ enhancements in M/MgB$_2$ (M=Ag, Cu and Nb) system at 20 K and 1 T were first observed in the sintered bulk samples with small amount of M. They were prepared from the mixture of Mg, B and M$_n$O$_m$ in the 10%H$_2$/Ar atmosphere at 900$^\circ$C for 30 minutes. The largest $J_c$ of M=Ag, Cu and Nb system were 1.33-, 1.48- and 1.70-times larger than that of pure MgB$_2$, respectively.

1. Introduction

Many authors have been tried to enhance the pinning force in the MgB$_2$ superconductor by the doping of several kinds of element. The critical current density $J_c$ at 20 K of liquid hydrogen temperature was about $10^4$ A/cm$^2$ for pure MgB$_2$ at 20 K [1]. Recently, the powder-in-tube (PIT) method to fabricate the super-conducting wires or tapes have been developed using Ag and Cu sheaths [2-5] in which the improved $J_c$'s of 2~3×$10^4$ A/cm$^2$ under 1T at 20K were observed without $T_c$-reduction. By scanning electron microscopy (SEM) measurement, the formation of Mg-Ag and Mg-Cu alloys were confirmed between MgB$_2$ cores and the sheath materials of Ag and Cu, respectively [3]. The improvement of $J_c$ was also reported for Nb-sheathed MgB$_2$ wires [6] and Nb$_x$B$_2$/MgB$_2$ tapes [7]. Therefore the addition of nano-particles of Mg-Ag or Mg-Cu alloys, or NbB$_2$ can be expected to form strong pinning centers in the sintered bulk samples of MgB$_2$.

2. Materials and method

The measured samples were sintered from the mixture of Mg-, B- and M$_n$O$_m$-powder, where M=Ag, Cu and Nb. The starting mole ratio was Mg : B : M=1.6(1-x) : 2(1-x) : 2(x) for M$_n$O$_m$ of Ag$_2$O or CuO. Meanwhile Mg : B : Nb=1.6(1-x) : 2 : x for Nb$_2$O$_5$ powder specimen. The excess amount of 0.6(1-x) for Mg was determined empirically to form high quality MgB$_2$ by the present method. The solid reaction of the powder mixture was performed in the electric furnace at 900 $^\circ$C for 30 minutes under Ar-atmosphere with 10%H$_2$ gas, followed by the rapid cooling. Then the above oxides were reduced to M by H$_2$/Ar gas at high temperature, and M reacted with Mg or B to form extrinsic pinning centers. We prepared the samples of $x$=0~0.05 for the present systems.

In figure 1, the CuK$_\alpha$ powder x-ray diffractions (XRD) are shown for the prepared samples, where the (101) peak intensities of MgB$_2$-phase were normalized to 100. For M=Ag system, the impurity of Ag$_3$Mg- and AgMg-particles with about 10-15 nm diameter were confirmed by the estimation using Scherrer's formula. Same results were also obtained by the transmission electron microscopy (TEM) observation. For M=Cu system, the MgCu$_2$ nano-particles were found, while NbB$_2$ impurity existed in
M=Nb system. Considering the small amount of MgO impurity, following chemical reactions were assumed as \((1-x)(1.6Mg+2B) + (x/m)M_{\text{total}}O_{\text{total}} \rightarrow (1-x)MgB_2 + xMMg + zMgO \uparrow wMg \uparrow\) for M=Ag or Cu system, where \(xy+z+w=0.6(1-x)\) and \(y\) is the averaged value of Mg for M-Mg alloy. For M=Nb system, \(1.6(1-x)Mg+2B + (x/2)Nb_2O_5 \rightarrow (1-x)MgB_2 + xNbB_2 + zMgO \uparrow wMg \uparrow\) where \(z+w=0.6(1-x)\).

Electrical resistivity \(\rho\) were measured by DC four terminals method between 20 K and 300 K. The magnetization measurements were performed by the Quantum Design’s MPMS SQUID magnetometer from 4 K to 100K between the field of \(-5\) T and 5 T. The expressions for magnetization by extended critical state model \([8-11]\) were fitted to these experimental data, and the \(J_c\)-values were estimated for each sample.

3. Results and discussion

The temperature dependence of resistivity \(\rho\) \((T)\) showed that the superconducting transition temperatures \(T_c\) (mid points) were about 39K for all of the samples. The absence of \(T_c\) reduction in our samples means the coexistence of pure MgB\(_2\)-phase and nano-particle like impurities, because the Ag atoms were unable to substitute with Mg atoms in MgB\(_2\) by the rapid sintering at high temperature of 900\textdegree{}-1000\textdegree{}C for 0.5\textdegree{}-2 hours \([12,13]\). The substitution of Ag atoms into Mg sites of MgB\(_2\) was realized by the sintering at relatively low temperature of 700\textdegree{}-950\textdegree{}C for a long time of 1\textdegree{}-15 hours \([14,15]\), when the large reduction of \(T_c\) by the chemical pressure was observed for the solid solution of Mg\(_{1-y}\)Ag\(_y\)B\(_2\) \([14]\). Little change of \(T_c\) was preferable to the pinning property in this system.

The critical current density \(|J_c(H)|\) was estimated by the equation of extended critical state model \([8-11]\) of \(|J_c(H)|=B_{eq}*\{B_{eq} + B_0\}/\{2\mu_0\{B_{eq}(H)+B_0\}\}\). In this equation, \(\mu_0\) of \(4\pi \times 10^{-7}\) [Tesla m/A] is the vacuum permeability, and \(2a\) is the thickness of slab sample. \(B_{eq}(H)\) of \(\mu_0[H+M_{eq}(H)]\) is the flux density at the sample surface, where \(M_{eq}\) is the equilibrium magnetization. \(B_{eq}\) represents \(B_{eq}(H_p)\), where \(H_p\) is the full penetration field above which the internal flux density, \(B_{int}\) becomes non-zero at the center of the slab. \(B_{eq}\) can be called as the cross-over flux density \([8-11]\) between Bean \([16]\) and Anderson-Kim \([17]\) states. Analyses of ZFC \(M(H)\)-curves were performed using equations given in
earlier papers [8-11]. The parameters $B_{eq}$, $B_0$ and the normalization factor $c$ were evaluated from the least square fitting of experimental $M(H)$-data to theoretical equations by the Gauss-Jordan method.

In figure 2, the experimental and theoretical $M(H)$-curves and $\mu_0aJ_c$-curves of $M=$Ag system were depicted for $x=0$ to 0.02 samples at 20 K. As shown in this figure, the improvement of $J_c$ was visible to the $x=0.01$ sample containing the Ag$_2$Mg- and AgMg-nano-particles. By the scanning electron microscopy (SEM), the accumulation of MgB$_2$ flakes with the thickness of about $1\sim2\times10^{-4}$ m was observed for all samples. If we use $10^{-4}$ m as $a$, $J_c$'s at 20 K and 1 T was estimated as $3.2\times10^4$, $4.2\times10^4$ and $3.6\times10^4$ A/cm$^2$ for $x=0$, 0.01 and 0.02 sample, respectively. Meanwhile the irreversibly field $H_{irr}$'s at 20 K were 4, 4 and 3.5 T for $x=0$, 0.01 and 0.02, respectively.

The $x$-dependences of $J_c$'s at 20K under 0 and 1T, normalized by the $J_c$ of pure MgB$_2$, were shown in figure 3. The $J_c(x)/J_c(0)$ at 20 K and 1 T had the highest value of 1.33 at $x=0.01$ for $M=$Ag, 1.48 at $x=0.03$ for $M=$Cu and 1.70 at $x=0.02$ for $M=$Nb system. The present report of enhancement of $J_c$ is the first one for $M/MgB_2$ ($M=$Ag, Cu and Nb) system.

![Figure 3. $x$-dependences of $J_c$'s at 20K under 0 and 1T, normalized by the $J_c$ of pure MgB$_2$.](image)

The previous studies of pinning property in Ag/MgB$_2$ system were performed for $x$ larger than 0.02 [12,13], and only negative results were obtained. We think that these poor $J_c$ results may be due to the production of another boride phase of MgB$_4$ at $x$ above 0.02. Therefore we can expect that the Ag content $x$ around 0.01 is a critical one for the pinning enhancement only by the existence of Ag/Mg nano particles as the strong pinning centers. In the systems of $M=$Cu and Nb, small amount of MgCu$_2$ near $x=0.03$ and NbB$_2$ near $x=0.02$, respectively, are also critical to give the strong flux pinning force and higher $J_c$.

Here it should be noted that the flux jumps at 5 K, being observed as irregular $M(H)$-curves in low field region, disappeared in the present Nb/MgB$_2$ system. It means that NbB$_2$ impurity may be useful to suppress the origin of flux jump which is the thermally excitation of dendritic flux avalanches in MgB$_2$ [18].

4. Conclusion

$J_c$ enhancements in $M/MgB_2$ ($M=$Ag, Cu and Nb) system were first observed in the sintered bulk samples with small amount of $M$. They were prepared from the mixture of Mg, B and $M_{2}O_3$ in the $H_210\%$/Ar atmosphere at 900 °C for 30 minutes. Produced Mg/Ag, Mg/Cu and NbB$_2$ particles are good pinning centers for the penetrating magnetic flux into MgB$_2$, because the size of these impurity
particles are comparable to the coherent length $\xi$ (~10 nm) of MgB$_2$. In the samples with larger amount of M, the impurity phase of MgB$_4$ probably interrupts the superconductive characteristics of MgB$_2$ itself. The enhancement of pinning property at 20 K and 1 T, and the suppression of flux jump at 5 K in low field in the M=Nb system is very remarkable functions to form high $T_c$ superconducting wires and tapes etc. Variation of flux distribution in our system is very interesting subject, and the magnetic optical experiment is now needed. Observed images of magnetic flux shall be reported elsewhere in the near future.

References

[1] Canfield P C, Bud'ko S L, Finemore D K 2003 An overview of the basic physical properties of MgB$_2$ Physica C 385 1-7.
[2] Glowacki B A, Majoros M, Vickers M E, Zeimet B 2002 Superconducting properties of the powder-in-tube Cu-Mg-B and Ag-Mg-B wires Physica C 372-376 1254-1257.
[3] Soltanian S, Wang X L, Horvat J, Li A H, Liu H K, Dou S X 2002 Improvement of critical current density in the Cu/MgB$_2$ and Ag/MgB$_2$ superconducting wires using the fast formation method Physica C 382 187-193.
[4] Zhou S, Pan A V, Ionescu M, Liu H, Dou S 2002 Influence of Ag, Cu and Fe sheaths on MgB$_2$ superconducting tapes Supercond. Sci. Technol. 15 236-240.
[5] Martínez E, Angurel L A, Navarro R 2002 Study of Ag and Cu/MgB$_2$ powder-in-tube composite wires fabricated by in-situ reaction at low temperatures Supercond. Sci. Technol. 15 1043-1047.
[6] Sumption M D, Peng X, Lee E, Tomsic M and Collings E W 2001 Transport current in MgB$_2$ based superconducting strand at 4.2 K and self-field Cond-mat/0102441.
[7] Nakane T, Takeya H, Fujii H and Kumakura H 2005 Effect of Nb,B$_2$ addition on the $J_c$-B characteristics of MgB$_2$ tapes Supercond. Sci. Technol. 18 521-525.
[8] Kimishima Y, Uehara M, Kuramoto T, Ichiyanagi Y, Iriyama Y and Yorimasa K 2002 Comments on magnetically estimated $J_c$ for MgB$_2$ by critical state models Physica C 377 196-201.
[9] Yorimasa K, Uehara M, Kuramoto K, Inoue H and Kimishima Y 2003 S-doping effects on pinning property of Bi2212 single crystals Physica C 392-396 306-310.
[10] Kimishima Y, Ichikawa H, Takano S, Kuramoto T 2004 Magnetization analysis of sintered Bi2223usin an extended critical state model Supercond. Sci. Technol. 17 S36-S41.
[11] Kimishima Y, Uehara M, Kuramoto T, Takano S, Takami S 2004 La-doping effects on pinning properties of MgB$_2$ Physica C 412-414 402-406.
[12] Jin S, Mavoori H, Bower C and van Dover R B 2001 High critical currents in iron-clad superconducting wires Nature 411 563-565.
[13] Sun T, Zhang X P, Zhao Y G, Shen R, Wang K, Zhang L W, Cao B S, Xiong Y H, Li P J and Wen H H 2002 Study of reactions between MgB$_2$ and Ag at high temperature Physica C 382 367-372.
[14] Cheng C H, Zhao Y, Wang L, Zhang H 2002 Preparation, structure and superconductivity of Mg$_{1-x}$Ag$_x$B$_2$ Physica C 378-381 244-248.
[15] Cheng C H, Zhao Y, Zhu X T, Vowotny J, Sorrell C C, Finlayson T, Zhang H 2003 Chemical doping effect on the crystal structure and superconductivity of MgB$_2$ 2003 Physica C 386 588-592.
[16] Bean C P 1964 Magnetization of high-field superconductors Rev. Mod. Phys. 36 31-39.
[17] Anderson P W, Kim Y B 1964 Hard superconductivity : theory of the motion of Abrikosov flux lines Rev. Mod. Phys. 36 39-43.
[18] Johansen T H, Baziljevich M, Shantzev D V, Goa P E, Galperin Y M, Kang W N, Kim H J, Choi E M, Kim M -S and Lee S I 2002 Dendritic magnetic instability in superconducting MgB$_2$ films Europhys. Lett. 59 599-605.