Water-Quenched Effects of 5 wt.% (Fe, Ti) particle-doped MgB$_2$ Superconductor and Low Limit of Pinning Effect

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Abstract

We have studied magnetic properties of water-quenched 5 wt.% (Fe, Ti) particle-doped MgB$_2$ comparing with that of air-cooled one. Generally, grain refinement is achieved by increasing cooling rate, which implies an increase of grainboundaries in the superconductor. Here we show that increased grainboundaries influence what kinds of effects on the field dependence of magnetization and what is the mechanism. As a result, they are served as a pinning center at a high field whereas they are served as a pathway to facilitate the movement of fluxes pinned on volume defects at a low field. As modeling grainboundaries in a superconductor, we explained that they had a flux pinning effect as well as the flux-penetrating promotion effect. As temperature increases, the pinning ability of a grainboundaries decreases, which was caused by increased coherence length. Stacking fault planes and twin boundaries have also been considered by using the model. It explained the reason for that stacking fault planes of MgB$_2$ do not have any pinning effect and the twin boundary of HTSC have the strong pinning or strong flux-penetration effect depending on the direction of the applied field.

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I. INTRODUCTION

MgB$_2$ has been known a superconductor which has a poor field dependence of magnetization [1–3]. In order to overcome this problem, we have been studying the properties of MgB$_2$ which were doped with (Fe, Ti) particles of which radius is 163 nm on average [4]. The best performance was obtained on 5 wt.% (Fe, Ti) particle-doped MgB$_2$ among the various specimens. Although the specimen showed considerable results, we still have the desire that diamagnetic property would be larger on the high field and the flux jump would be more relaxed on the low field. To achieve this purpose, we chose water-quenching (WQing) method.

Generally, if a WQing is carried out for materials, there is no time for a particle to grow due to the rapid cooling rate. Thus, grains of the material become finer, and grain-boundaries (GBs) of the material increased. Increased GBs means increasing the number of weak pinning sites in the superconductor. Concerning GBs as a pinning site, they are not only interconnected, but also connected on volume defects. Thus, pinned fluxes at a volume defects would leak out easily along the GBs in the superconductor, and the leak-out fluxes would move into the superconductor easily along GBs.

When kinds of defects are changed in the superconductor, they cause a diamagnetic property and a field dependence of magnetization to change. These results have been shown in many superconductors, and the representative example is MgB$_2$ single crystal and melt-textured growth (MTG) specimens of high temperature superconductor (HTSC) [5, 6]. Their field dependence of magnetization (M-H curve) are completely different from that of bulks, and these behaviors are determined to be due to differences in dominant defects caused by production method.

We have understood that planar defects which include GBs are weak pinning sites. However, if we think them simply weak pinning sites, we cannot explain the phenomena which are fishtail effect of HTSC single crystal and no pinning effect of MgB$_2$ single crystal. We think that the former is related with twin boundaries and the latter is stacking fault planes. In addition, it have to be empathized that GBs are a pathway to promote movement of fluxes in superconductor, which is the most in pinned fluxes at volume defects. In this study, we investigated magnetic properties of water-quenched 5 wt.% (Fe, Ti) particle-doped MgB$_2$ comparing with that of air-cooled one and tried to understand the reason for that stacking
fault planes of MgB$_2$ do not have any pinning effect and the twin boundary of HTSC have the strong pinning or strong flux-penetration effect depending on the direction of the applied field.

II. RESULTS AND DISCUSSION

A. Effects of water-quenching

Figure 1 shows field dependences of magnetization (M-H) curves at 5 K, which are that of 5 wt.% (Fe, Ti) particle-doped MgB$_2$ specimens cooled in air and quenched in water, respectively. Pure MgB$_2$ are used as a reference, which was cooled in air. After doping 5 wt.% (Fe, Ti) particles on MgB$_2$, the field dependence of the specimens have improved greatly regardless of cooling methods. On the other hand, there was a significant difference in the M-H curves between 5 wt.% (Fe, Ti) specimens according to cooling methods. The first is that there was a magnetization difference on the high field, which is that $\Delta M$ of WQed specimen is much larger than the counterpart in magnetic field above 2.5 T. And the second is that the diamagnetic crossover of the two specimens is occurred around 2.5 Tesla (T). It means that the air-cooled (ACed) specimen has a large $\Delta M$ under 2.5 T whereas WQed specimen has a larger $\Delta M$ over 2.5 T.

What is the reason for that $\Delta M$ of WQed specimen is smaller in lower field whereas it is larger in higher field compared to ACed specimen?. We understand that this behavior is caused by increasing GBs due to the WQing. As mentioned above, GBs are not only interconnected, but also connected at volume defect. The free energy density of a volume defect is much lower than that of the planar defect due to its own volume, thus it can pin many fluxes. When many fluxes are pinned at a volume defect, the free energy density of it would increase and pinned fluxes are easier to escape from the defect at small fluctuation.

Thus, they would leak out from the volume defect through the GBs if the volume defect pin the fluxes many enough because the GBs are connected to the volume defect. The more GBs are connected at the volume defect, the more easily some of the pinned fluxes at the volume defect can leak out from the volume defect through GBs. Leak-out fluxes from the volume defect means that the fluxes move into an inside of the superconductor. Therefore, the flux pinning limit of the volume defect decreases as the number of GB increases. When
pinned fluxes move into an inside of the superconductor, magnetic induction (B) increase and diamagnetic property (M) also decreases by $4\pi M = B - H$.

On the other hand, as applied field increases, all of the volume defects in the superconductor reached their pinning limits because they pinned the fluxes preferentially which was caused by that pinned fluxes at volume defects bent like bow [7]. If applied field increases more, the volume defect no longer pin more fluxes. From this field, the grain boundary begins to show its effect as a barrier for the movement of fluxes. Of course, there is also a pinning effect of GBs at low field. However, the fluxes leaked out from the volume defect through GBs are only visible in M-H curve because pinning effect of volume defects is very strong at low field. Since the volume defect of ACed specimen begin to be weakened as a pinning center from 1.5 T (2 T for WQed specimen) and the pinning effects of GBs are clearly seen after 2.5 T as shown Fig. [1] (a). It is noted that total pinning effects by GBs in WQing is more than twice, compared to that in ACing when considered at 6 T in the figure.

For proving flux pinning effect and flux-penetrating promotion effect of GBs, let’s assume that there are GBs in the superconductor as shown in Fig. 2 (a). When the external magnetic field is applied along y-axis, quantum fluxes in the superconductor move along x-axis as shown in the figure. If the fluxes move through GB plane that are in parallel with their direction of movement, they would act as a pathway to penetrate the fluxes into an inside of the superconductor rather than pinning center to pin the fluxes.

However, they would serve as a pinning center when the fluxes move perpendicular to the GB plane (when the longitudinal direction of the flux and the plane direction of the GB are parallel). Thus, pinning force of a GB is $F_0d\cos \theta$ if the angle between the flux line and GB plane is $\theta$ as shown in Fig. 2 (a), where $F_0$ is the pinning force density of a GB when the $\theta$ is 0 and $d$ is width of GB. On the other hand, the effects of flux-penetrating promotion is equal to $P_0d\sin \theta$, where $P_0$ is flux penetration rate which is 1 in normal state.

This phenomenon is clearly observed in Fig. 1 (a). When the external field is less than 1.5 T, the ACed specimen is almost parallel with horizontal line, whereas the WQed specimen is slightly angled with the horizontal line. This means that the pinned fluxes on the volume defects in the WQed specimen leaked out from the volume defect more easier than that of the AC specimens owing to increased GBs, and the leak-out fluxes easily penetrate an inside of the superconductor along GBs. Therefore, the amount of penetrated fluxes (B) into the superconductor increases, and the diamagnetic property decreases. This behavior is more
pronounced at 10 K.

Figure 1 (b) shows M-H curves at 10 K, which are that of 5 wt.% (Fe, Ti) particle-doped MgB$_2$ specimens cooled in air and quenched in water, respectively. The crossover point of the two specimens is occurred around 2.5 T, which is similar with that of 5 K. However, inspecting entire M-H curve, the crossover point moved a quite higher field. This means that the influence of the pinning effect by GBs on the overall flux pinning is reduced at 10 K compared to that at 5 K. This behavior is demonstrated by the fact that the coherence length ($\xi$) increases as the temperature increases. The increased $\xi$ results in a reduction of the number of flux quanta that are pinned on GB when GB is wide enough to pin many fluxes or decreased ratio of a flux quantum when GB pins a flux quantum, which also reduce the influence of the GB pinning.

B. A model of grain boundary pinning in superconductor

A model is proposed to quantify the pinning effect and the flux-penetrating promotion effect of GBs. Figure 2 (b) is a modified suggestion of Fig. 2 (a). GBs of square shape is formulated as properties of $\sin\theta$ and $\cos\theta$ are summed respectively. Let’s assume that the size of the grains is constant, the thickness of the GB is $d$ and $d'$, and the length of a side of the grain is $2r$ as shown in the Fig. 2 (b). Assuming GBs as a square shape, we could understand more clearly the pinning effect of GB and the flux-penetrating promotion effect of GB. If $d$ is same as $d'$, the flux pinning effect and the flux-penetrating promotion effect are also increased as $d$ increases (generally, $d$ and $d'$ are the same at GBs and different at twin boundaries).

It is known that the coherence length ($\xi$) follows the equation

$$\xi(T)^2 \propto \frac{1}{1-t}$$

where $t = T/T_c$ [8]. Table 1 shows the variation of coherence length along temperature and ratios of a pinned quantum flux at GB when the width of GB can pin single flux quantum. It was assumed that $H_{c2}$ of the superconductor is 65.4 T at 0 K and $T_c$ is 37.5 K [9]. As shown in the table, the pinning effect of GB would drop sharply as temperature increases. On the other hand, the effect of flux-penetrating promotion increases as temperature increases because superconductivity of the specimen decreases and coherence length increases as temperature
increases. Therefore, flux movement in the superconductor are much easier as temperature increases if GBs increase.

The behavior predicted by the model is confirmed by Fig. 3 and Fig. 4. Figure 3 (a) is M-H curves at 15 K, which are that of 5 wt.% (Fe, Ti) doped MgB$_2$ specimens cooled in air and quenched in water, respectively. At this temperature, M-H curves of the two specimens almost overlap, but the diamagnetic properties of the WQed specimen are slightly larger in the field over 2.5 T, which means that GBs pinning is still remains at the temperature. As the temperature increases up to 20 K (Fig. 3 (b)), diamagnetic property of the ACed specimen is larger than that of WQed specimen in entire field except the low field. From these results, we can understand that flux-penetrating promotion effect was larger than pinning effect of GBs at 20 K.

The tendency is more pronounced at 25 K. Figure 4 (a) shows that the diamagnetic property of the ACed specimen are much larger than that of the WQed specimen over the entire field at 25 K. The decrease of diamagnetic property of the WQed specimen is too great to compare with that of ACed specimen. It is much more pronounced at 30 K (Fig. 4 (b)). The diamagnetic property of water-quenched 5 wt.% (Fe, Ti) doped MgB$_2$ specimens show worse than that of ACed pure MgB$_2$ specimen. This behavior is caused by that GBs do not play a role as a pinning center but plays a role of flux-penetrating promotion pathway owing to increased coherence length. It is noted that the maximum diamagnetic property of ACed doped specimen at 30 K are still not significantly different from the maximum diamagnetic property of other temperatures.

C. Discussion

Figure 5 shows GBs and stacking fault plain of MgB$_2$. The width of GBs is approximately 1 nm because the radius of Mg is 0.15 nm [10]. Hence, the pinning by GBs is too weak to be observed because coherence length of MgB$_2$ is 2.24 nm when $H_c$ is 65.4 T at 0 K. However, we already confirmed that the pinning effects of GBs are evident at 5 K and 10 K as shown in Fig. 1. This discrepancy can be analyzed in two ways. One is that the coherence length have to be shorter than 2.24 nm. However, there was no report that $H_c$ can exceed 68.6 T and coherence length does not decrease significantly even if $H_c$ is 68.6 T, which is 2.19 nm [11–13]. The other is that the width of GB have to be extended for the concept of
superconductivity. The latter means that the flux pinning by GB is not only confined to GB in the concept of material science, but neighborhood atoms of GB also have to be involved.

It should be noted that a GB has an empty space between Mg atoms as shown in Fig. 3(a). Considering that the superconducting phenomenon depends on the mutual vibrations of the atoms, they do not maintain the proper superconducting state because of the increased interatomic distance although atoms around a GB maintain the similar crystal lattice structure of MgB$_2$. In order that GB may get the flux pinning effect properly, the width of the GB must be extended enough to cause a flux quantum to completely fall into the GB, which includes at least the area that coherence length is the radius ($2\pi \xi^2$).

Thus, the non-superconducting region around the grain boundary must extend to at least 6 Mg atoms on both sides for that a flux quantum can be pinned completely. Therefore, it is hard to imagine that several fluxes are simultaneously pinning at a GB in the current experiments. Therefore, we thought that a flux quantum can be partially pinned at a GB of MgB$_2$, which results in that the pinning effect of GBs decreases sharply as temperature increases. On the other hand, stacking fault plane of MgB$_2$ have the width of 0.6 nm as shown Fig. 5(b) and it is anticipated that there was no pinning effect at all. The anticipation is caused by the fact that the non-superconducting width of stacking fault plain was not significantly expanded over 0.6 nm because there is almost no space between Mg atoms.

On the other hand, there is a superconductor that $d$ is 0 in the Fig. 2(b), which is twin boundary plane in HTSC single crystal [14]. Because they have a direction, they exhibit strong pinning effect or strong flux-penetrating promotion effects depending on a direction of the applied field. If twin boundary plane is perpendicular to the moving direction of the fluxes, (if the longitudinal direction of the fluxes and the twin boundary plane are parallel), strong pinning effects occurs. However, if the $\theta$ between twin boundaries and the moving direction of the fluxes in SC decreases, flux-penetrating promotion effect increases [15, 16].

We were surprised at the M-H curve of MgB$_2$ single crystal when it was reported [5, 17]. The curve was similar to that of ideal superconductor which has no pinning effect. The authors did not know the reason and stated that composition of the MgB$_2$ SC was determined to be MgB$_{1.9}$. MgB$_2$ is the superconductor synthesized by penetrating boron into Mg crystal structure at high temperature, thus stacking fault planes inevitably exist to reduce stacking stress of MgB$_2$ if it is made as single crystal [18]. The stacking fault planes formed on the MgB$_2$ SC are not directional. It is determined that the width of stacking fault plane is
maximum 0.6 nm as mentioned, which is much shorter than coherence length of MgB$_2$ (2.24 nm at 0 K when H$_c2$ of MgB$_2$ is 65.4 T). Therefore, there is almost no flux pinning effect, but the only flux-penetrating promotion effect is. Therefore, the M-H curves of MgB$_2$ single crystal are similar to those of an ideal state that the pinning effect does not occur at all.

III. CONCLUSION

We studied water-quenched 5 wt.% (Fe, Ti) particles-doped MgB$_2$ specimen and compared with air-cooled specimen for flux pinning effects caused by increased GBs. The diamagnetic properties of water-quenched specimen was rather lower than that of air-cooled specimen in the low-magnetic field under low temperatures (5 K and 10 K). It was because GBs are served as a pathway leaking out the fluxes pinned on the volume defects. On the other hand, diamagnetic properties by grain boundary pinning increased under higher magnetic field (more than 2.5 T), which is caused by that GBs are served as pinning center. The increased coherence length of the superconductor at high temperatures resulted in a significant decrease of the flux-pinning effect compared to the air-cool specimen. A model of the flux-pinning effects of grain boundary revealed that it has a flux-pinning effect and a flux-penetrating promotion effect simultaneously. Stacking fault planes and twin boundaries have also been considered by using the model. It explained that stacking fault planes of MgB$_2$ do not have any pinning effect and the twin boundary of HTSC have the strong pinning or strong flux-penetration effect depending on the direction of the applied field.

IV. METHOD

Pure MgB$_2$ and (Fe, Ti) particle-doped MgB$_2$ specimens were synthesized using the nonspecial atmosphere synthesis (NAS) method [19]. Briefly, NAS method needs Mg (99.9% powder), B (96.6% amorphous powder), (Fe, Ti) particles and stainless steel tube. Mixed Mg and B stoichiometry, and (Fe, Ti) particles were added by weight. They were finely ground and pressed into 10 mm diameter pellets. (Fe, Ti) particles were ball-milled for several days, and average radius of (Fe, Ti) particles was approximately 0.163 µm [7]. On the other hand, an 8 m-long stainless-steel (304) tube was cut into 10 cm pieces. Insert holed Fe plate into stainless- steel (304) tube. One side of the 10 cm-long tube was forged
and welded. The pellets and pelletized excess Mg were placed at uplayer and downlayer in the stainless-steel tube, respectively. The pellets were annealed at 300 °C for 1 hour to make them hard before inserting them into the stainless-steel tube. The other side of the stainless-steel tube was also forged. High-purity Ar gas was put into the stainless-steel tube, and which was then welded. Specimens had been synthesized at 920 °C for 1 hour and quenched in water. The field and temperature dependence of magnetization were measured using a MPMS-7 (Quantum Design). During the measurement, sweeping rates of doped specimens were applied equally for the same flux-penetrating condition.

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FIG. 1: Field dependences of magnetization (M-H curves) of water-quenched specimen and air-cooled specimens. (a): M-H curves at 5 K. (b): M-H curves at 10 K.
FIG. 2: Schematic representations of grain boundary pinning. (a) General grain boundary. (b) Modified grain boundary.
FIG. 3: Field dependences of magnetization (M-H curves) of water-quenched specimen and air-cooled specimens. (a): M-H curves at 15 K. (b): M-H curves at 20 K.
FIG. 4: Field dependences of magnetization (M-H curves) of water-quenched specimen and air-cooled specimens. (a): M-H curves at 25 K. (b): M-H curves at 30 K.
FIG. 5: Schematic representations of grain boundary and stacking fault plain of MgB₂. (a): Grain boundary of MgB₂. (b): Stacking fault plain of MgB₂. Black circles are boron and white circles are magnesium.
TABLE I: The fraction of pinned fluxes on a planar defect along the temperature. It is assumed that $H_{c2}$ of the superconductor is 65.4 T at 0 K and $T_c$ is 37.5 K and the width of grain boundary can pin a flux quantum.

| Temperature | 0 K | 5K | 10 K | 15 K | 20 K | 25 K | 30 K | 35 K |
|-------------|-----|----|------|------|------|------|------|------|
| Coherence length (nm) | 2.24 | 2.41 | 2.62 | 2.90 | 3.29 | 3.89 | 5.02 | 8.29 |
| The fraction of pinned fluxes on the grain boundary: $\left(\frac{\xi_0}{\xi_K}\right)^2$ | 1 | 0.86 | 0.73 | 0.60 | 0.47 | 0.33 | 0.20 | 0.07 |