Strong Relationship between Irreversibility Field and Crystallinity Discovered in Undoped and Carbon Substituted MgB₂ Bulks

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Abstract. The relationship between irreversibility field, $H_{irr}$, and crystallinity of MgB₂ bulks including SiC or B₄C doped samples was studied. Among the XRD peaks of MgB₂, the FWHM of (110) reflection corresponding to the in-plane disorder was strongly dependent on the samples and $H_{irr}$ was found to be systematically increased with an increase of the FWHM of MgB₂ (110) peak. Enhanced intra-band scattering and strengthened grain boundary flux pinning are suggested to contribute to the excellent $H_{irr}$ characteristics. On the other hand, weak correlation between $H_{irr}$ and FWHM of (002) peak was confirmed. These mean that introduction of disorders into the $ab$-plane, i.e., distortion in honeycomb boron sheet, is essentially effective to enhance $H_{irr}$.

1. Introduction

The 40 K-class $T_c$ of MgB₂ enabled its practical use at high operating temperatures around 20 K [1]. MgB₂ shows higher upper critical field, $H_{c2}$, than that of conventional Nb-based superconductors, such as NbTi and Nb₃Sn. In particular, very high $H_{c2}(0)$ exceeding ~50 T has been reported for moderately alloyed thin films [2,3]. However, critical current properties of MgB₂ bulks, wires and tapes are suppressed rapidly by magnetic fields due to low irreversibility field, $H_{irr}$, and poor flux pinning. Compared to the other metallic superconductors, the $H_{irr}$ of MgB₂ is apparently lower than $H_{c2}$. Enhancements of $H_{irr}$ and critical current density, $J_c$, in magnetic fields are needed for extensive applications at ~20 K under high fields. Among the numerous approaches to improve flux pinning properties of MgB₂ by chemical method, doping of carbon [4] or carbon contained compounds, such as B₄C [5] and SiC [6,7], is well known to be most effective, while detailed mechanisms of the improved $J_c$ characteristics by carbon substitution have not been well clarified yet.

On the other hand, crystallinity of samples is one of the determining factors of $H_{c2}$, $H_{irr}$ and $J_c$ under high fields. Crystallinity dependent $H_{c2}$ and $H_{irr}$ were found for MgB₂ bulks synthesized by various heating conditions, which have various full-width at half-maximum (FWHM) values derived from powder X-ray diffraction (XRD) peaks [8,9]. Disordered crystal lattice caused by various types of lattice defects or intragranular precipitates are the origin of degraded crystallinity. These disorders in grains certainly enhance the interband and intraband scattering in $\sigma$, $\pi$ bands, and moderate increase of intraband scattering directly results in an improvement of $H_{c2}$ through a reduction of coherence length.
Furthermore, flux pinning by electron scattering at grain boundaries is theoretically expected to be enhanced by moderate reduction of mean free path, i.e., degradation of crystallinity [10].

In the present paper, the relationship between the lattice properties and critical current properties of undoped and carbon substituted MgB$_2$ bulks were studied. Carbon substitution is found to be effective for improvement of $H_{irr}$ through the introduction of disorders into the $ab$-plane. Our results strongly suggest that the observed positive effects of carbon substitution on the critical current properties of MgB$_2$ are simply explained by the degradation of crystallinity.

2. Experimental

MgB$_2$ bulks were synthesized by the PICT (Powder-In-Closed-Tube) method [11]. Powders of magnesium (99.5% purity), boron (99.9%), graphite (99.9%), SiC (99.9%) and B$_4$C (99.9%) were used as starting reagents. Both ends sealed SUS316 tubes filled by the powder mixture with nominal compositions of MgB$_2$, MgB$_{2-x}$C$_x$, MgB$_{2-x}$(SiC)$_x$, and MgB$_{2-5x}$(B$_4$C)$_x$ ($x=0-0.4$) for undoped, graphite doped, SiC doped and B$_4$C doped samples, respectively, were uniaxially pressed into tape shape. The raw tapes were typically heated at 600-950°C for 3-24 h in evacuated quartz ampoules, and then followed by quenching to room temperature.

Lattice parameters and crystallinity of the samples were analyzed by the powder X-ray diffraction (XRD) method using Cu-$K_a$ radiation. Magnetization of the bulk samples was measured by a SQUID magnetometer (Quantum Design: MPMS-XL5s). $J_c$ was calculated from width of magnetization hysteresis loops based on the extended Bean model.

3. Results and discussion

3.1. Carbon substitution effects on crystal lattice of MgB$_2$

Influence of carbon substitution on lattice parameters and crystallinity were systematically investigated for the graphite doped MgB$_2$ samples. Figure 1(a) shows the relationship between carbon substitution level $x$ and lattice parameters $a$ and $c$ for the MgB$_{2-x}C_x$ samples heated at 950°C for 12 h.

Figure 1. The carbon substitution level dependence of lattice parameters $a$ and $c$ (a), FWHM of MgB$_2$ (110) and (002) reflections (b), for the graphite doped MgB$_{2-x}C_x$ bulks.
Systematic decrease of lattice parameter $a$ with an increase of doping level $x$ was observed, while lattice parameter $c$ kept almost unchanged. The relationships between FWHM values of in-plane (110) and out-of-plane (002) peaks and doping level $x$ are shown in figure 1(b). Significant broadening of the FWHM of (110) reflection, i.e., degradation of in-plane crystallinity, was observed in carbon substituted samples. Difference in ionic radii of boron (0.027 nm) and carbon (0.016 nm) is believed to decrease the $a$-axis length accompanying the in-plane lattice distortion. On the other hand, quite small influence on the out-of-plane FWHM of (002) reflection by carbon substitution was confirmed. The behaviors of the FWHM by carbon substitution are obviously corresponding to those of lattice parameters. These results indicate that carbon substitution on boron site affects mainly in-plane structure. This selective role of carbon substitution is in contrast to aluminum substitution on magnesium site which decreases both $a$ and $c$, and broadens both (110) and (002) reflections.

3.2. Crystallinity and irreversibility field in carbon substituted MgB$_2$

Magnetization measurements revealed that $T_c$ of the carbon substituted samples decreases with an increase of carbon doping level. $J_c$, calculated from the hysteresis loop was typically 2-4×10$^5$A/cm$^2$ under low fields at 20 K for both undoped and carbon substituted samples. Detailed results will be found elsewhere [9,10]. The relationship between $H_{irr}$ defined by a $J_c$ criterion of 10$^3$ A/cm$^2$ and the FWHM of (110) and (002) peaks of MgB$_2$ are shown in figures 2 (a) and (b), respectively. Strong correlation between the FWHM of (110) peak and $H_{irr}$ are clearly seen. This result directly means that introduction of disorders into the $ab$-plane, i.e., distortion in honeycomb boron sheet, is essentially effective to enhance $H_{c2}$ and $H_{irr}$. On the other hand, less prominent correlation between $H_{irr}$ and the FWHM of (002) peak was observed especially for carbon substituted samples.

The particular electronic structure of MgB$_2$ is suggested to contribute to these results. From band calculations [12], 3D metallic $\pi$-band from boron $p$ orbitals has a strong $ab$-plane distribution and a certain degree of interlayer distribution. On the other hand, 2D covalent $\sigma$-band from boron $sp^2$ orbitals has an extremely weak distribution along $c$-axis direction, while interlayer distribution is large reflecting the boron $p_{xy}$ orbital. Therefore, broadening of the (110) reflection, i.e., buckling of $ab$-plane

![Figure 2. Relationships between irreversibility field at 20 K and FWHM of MgB$_2$ (110) peak (a), MgB$_2$ (002) peak (b) for the undoped and B$_4$C or SiC doped (carbon substituted) MgB$_2$ bulks. Samples with $T_c$>35 K were selected for the carbon substituted samples.](image-url)
is considered to be directly linked to scattering of electrons in $\sigma$ and $\pi$ bands. On the other hand, broadening of the (002) reflection may be caused by weak scattering only in $\pi$ band, because of the small interlayer distribution in $\sigma$ band. Although the FWHM of (110) and (002) usually correlates each other and observed $H_{irr}$ dependence of the FWHM of (002) is considered to be due to broadening of FWHM of (110) for the undoped MgB$_2$, the carbon substituted samples do not show clear dependence of $H_{irr}$ on FWHM of (002). This strongly indicates that the in-plane lattice was selectively disordered by the carbon substitution.

Improved $H_{irr}$ observed in B$_4$C and SiC doped samples with larger FWHM similarly in the case of undoped samples directly suggests that enhancement of $H_{irr}$ by carbon substitution is attributed to the strengthened electron scattering flux pinning at grain boundaries. Since substituted carbon atoms do not act as strong pinning centers, $H_{irr}$ is suggested to be determined by the same pinning mechanism as in undoped MgB$_2$. Increased intra-band scattering in $\sigma$ and $\pi$ bands introduced by carbon substitution, which enhances $H_{c2}$, also improves the grain boundary flux pinning. Therefore, the carbon substitution effect on the enhanced critical current properties might be simply explained by the introduction of lattice disorders into MgB$_2$ grains, in other words, degradation of crystallinity.

4. Conclusions

The relationship between $H_{irr}$ and crystallinity of undoped and carbon substituted MgB$_2$ bulks was studied. $H_{irr}$ was found to be systematically increased with an increase of the FWHM of MgB$_2$ (110) peak. Enhanced intra-band scattering and strengthened grain boundary flux pinning are considered to contribute to high $H_{irr}$ observed in samples with large FWHM of (110). On the other hand, weak correlation between $H_{irr}$ and FWHM of (002) peak was confirmed. These mean that introduction of disorders to the $ab$-plane, i.e., distortion in honeycomb boron sheet, is essentially effective for the enhancement of $H_{irr}$. We conclude that the effects of carbon substitution on critical current properties are clearly explained from the view point of crystallinity.

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