Improved critical current properties of MgB2 bulks by controlling microstructures

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Abstract. Effects of controlled grain size on the critical current properties of in-situ fabricated polycrystalline MgB2 bulks were systematically investigated. Grain sizes of MgB2 bulks were controlled by three different methods: changing the heating conditions, such as temperature and holding time, changing the molar ratio between Mg and B, and starting from B powders with different grain sizes. MgB2 bulks with smaller grain sizes were obtained when heating at low temperatures or for short time at high temperatures starting from fine B powder. Small MgB2 grains were also found in the bulks starting from Mg-deficient composition using fine B powder. Through the careful analyses on the grain size of MgB2 and critical current properties, we found that MgB2 bulks with smaller grain sizes exhibit higher irreversibility fields and larger maxima of pinning force density. Our present results supported the scheme that grain boundaries are the predominant pinning centres in polycrystalline MgB2 bulks.

1. Introduction

The critical current ($J_c$) properties of MgB2 materials have improved year by year since the discovery of superconductivity of MgB2 in 2001[1]. The good grain connectivity and the high $T_c$ of 39 K allow MgB2 to be widely used like Nb-Ti or Nb3Sn as polycrystalline conductors at higher temperatures of 15-20 K. Although chemical doping has been the major approach to improve its low $J_c$ of polycrystalline bulks under high magnetic fields, control of microstructure should also be essential for MgB2, since $J_c$ properties of similar metallic superconductors Nb3Sn and V3Ga have dramatically improved by controlling microstructures. However, there have been few systematic studies on the direct relationship between $J_c$ properties and microstructures of undoped polycrystalline MgB2 bulks.

In the case of Nb3Sn, grain boundaries are almost confirmed to be the predominant pinning sites [2]. The most generally accepted source of grain-boundary pinning is electron scattering. According to Zerweck [3], electron scattering at grain boundaries decreases the mean free path and consequently leads to a local decrease of the coherence length $\xi$. It causes an increase in the term $d\kappa / \kappa (\kappa = \lambda / \xi$, $\kappa$: Ginzburg-Landau constant, $\lambda$: penetration depth) in G-L equation for condensation energy, to result in a pinning effect for magnetic flux. This implies that the total pinning force per volume can be controlled either by degrading crystallinity of each grain, or by increasing density of grain boundaries.

Gupta et al. have proven that grain boundary is able to act as a pinning centre in MgB2, from angular dependence of $J_c$ of c-axis oriented thin film consisting of columnar crystals, and calculated its pinning potential [4]. By ball-milling of commercial MgB2 powder, $J_c$-properties of ex-situ MgB2...
bulks are improved [5]. Giunchi et al. have presented that $J_c$ properties change with grain size of *in-situ* MgB$_2$, by employing two B powders with different grain sizes as a starting powder [6]. We have shown that $H_{irr}$ strongly depends on sintering temperature, and observed a universal relationship between $H_{irr}$ and crystallinity in undoped and carbon-doped MgB$_2$ [7]. In the present study, we have attempted to clarify the essential effects of grain-size control on $J_c$ properties for MgB$_2$ polycrystalline bulks, which had not been well understood yet.

2. Experimental
Mg powder (325mesh: <45 μm, 99.9% in purity) was mixed with B powder under argon atmosphere. Approximately 0.15g of the mixture was placed in a SUS316 tube (3.0 mm in diameter, 0.2 mm in thickness, 100 mm in length) and pressed into a tape shape at 380 MPa. To prevent loss of Mg vapour, both ends of the tube were closed by bending and pressing. Heat-treatment was carried out in an evacuated quartz ampoule to react Mg with B to form MgB$_2$. The sample was then quenched to room temperature. Samples with different grain sizes were prepared by varying the heating temperature (630, 660, 700, 800, 850, 900°C), the holding time (1.5, 3, 6, 12, 24, 48 h), the grain sizes of starting boron powder (Boron A: 99.5%, crystalline, 1-45 μm in diameter; Boron B: 99%, amorphous, 0.5–1 μm in diameter; Boron C: 99.99%, amorphous, 0.05-0.1 μm in diameter.) and the nominal composition of Mg: B (0.9-1.0: 2.0). After the heat-treatment, the MgB$_2$ bulks were obtained by removal of the sheath.
Constituent phases were identified by powder XRD analysis. $T_c$ and $J_c$ properties of the resulting bulks were examined by magnetization measurements for samples with typical dimensions of 1.2 x 1.2 x 0.6 mm$^3$, using a SQUID magnetometer (Quantum Design MPMS-XL5s). $J_c$ was calculated from the width of magnetization hysteresis based on the extended Bean model. Irreversibility field ($H_{irr}$) was defined as the magnetic field where $J_c$ decreases down to 100 Acm$^{-2}$. Pinning force ($F_p$) was determined from the relationship $F_p = \mu_0 J_c H$.

Samples were fractured perpendicularly to tape surface and observed by SEM (KEYENCE VE-7800) equipped with EDX spectrometer (EDAX 7750/55 ME). Edges and boundaries of each MgB$_2$ grain were traced and fitted with an ellipse, to define its grain size as an average of its major and minor axes lengths. Any voids and impurity particles (mostly MgO and unreacted B) were avoided from the analysis. Nano-structures of pulverized samples were also studied by TEM (JEOL 2010F).

3. Results and discussion

3.1. XRD patterns
Completion of reaction was confirmed from the disappearance of diffraction peaks from Mg, to all samples prepared from Boron B and C by heating for 1.5–48 h at 900°C. Samples from Boron A heated for less than 24 h contained certain amounts of Mg, indicating that the reactions were incomplete. Samples prepared from Boron C heated at 630–900°C for 3 h or 48 h completed the reaction. Trace amounts of MgO were detected as an impurity phase in most samples. Intensities of peaks from MgO increased with the sintering temperature and time. These peaks were not detected in starting Mg powder, and were very broad in samples sintered at low temperatures near the melting point of Mg (650°C).

3.2. Transition temperatures
Transition temperatures were as high as 37 ~ 39 K in all samples even for Mg deficient ones. Samples sintered at lower temperatures exhibited slightly lower $T_c$, implying some influence of heating temperature to bulk crystallinity.
3.3. Typical microstructures
All samples contained flat voids parallel to the tape surface, 5-40 µm in diameter and 0.5-5 µm in thickness, resembling the shapes of pressed Mg grains before heating. Inner wall of each void was covered with a polycrystalline crust with 0.1-0.5 µm thick composed of fine MgO grains, which was confirmed by EDX analysis. These suggested that the voids were formed as a result of migration of Mg into B grains to form MgB$_2$, leaving empty crusts of MgO that had covered the Mg grains. Among these voids, we found grains of MgB$_2$ strongly connecting with each other. The MgO crust was terminating crystal growths of some MgB$_2$ grains. From TEM study, samples with very broad MgO peaks in the powder XRD patterns were found to contain fine MgO crystals 2-5 nm in diameter.

3.4. Results of grain-size control
Crystal growth rate of MgB$_2$ was observed to increase with the temperature of heat-treatment. Mean grain sizes of samples heated at 900°C rapidly increased with time, while samples heated below 700°C underwent very small changes in grain size within 48 h. This crystal growth was suppressed when Mg was mixed with B in an Mg-deficient ratio 0.9: 2.0. Grain sizes of MgB$_2$ were also strongly dependent on the initial particle sizes of B powder, and Boron C with smallest B particles gave smallest MgB$_2$ grains in all heating conditions examined. Very large B particles in Boron A turned into multi-domained MgB$_2$, and sizes of the domains increased with heating time. Through grain-size controls by heating temperature, time, Mg: B ratio and sizes of starting B powder, we succeeded to prepare MgB$_2$ bulks with mean grain sizes ranging from 0.1 to 3 µm.

3.5. Irreversibility fields and maximum pinning forces
Figures 3 (a) shows decreases in $H_{irr}$ with increasing heating time. Samples prepared from smaller B powder exhibited higher $H_{irr}$ than ones prepared from larger B powders, except for samples prepared from Boron A where reaction is incomplete. Figure 3 (b) shows decreases in $H_{irr}$ with increasing heating temperature. The decreases in $H_{irr}$ by high-temperature synthesis were suppressed by preparation in Mg-deficient conditions. So, in all series of samples, $H_{irr}$ was found to decrease with an increase of grain sizes. Figure 4 (a) shows a clear correlation between $H_{irr}$ and an inverse of mean grain size ($g^{-1}$), indicating that samples with smaller grain sizes have higher $J_c$ under high fields. We made a similar plot for $F_p^{max}$ since it is thought to directly reflect the density of effective pinning
centres. The linear relationship between $F_p$ and $g^{-1}$ was found as shown in Fig. 4(b). Dispersion in values of $F_p$ are probably caused by the imperfectness of grain connections due to short heating time. Higher and more correct values for $F_p$ will be achieved by preparing samples with better grain connections, and elimination of voids due to Mg particles.

Conclusion

Polycrystalline MgB$_2$ bulks with different grain sizes were successfully prepared by controlling sintering temperature, sintering time, nominal composition of Mg: B and particle sizes of starting B powder. By any of above grain-size control methods, irreversibility fields were improved with decreasing grain sizes of MgB$_2$. A linear correlation between $F_p$ and inverse of grain sizes implied that grain boundary pinning is the predominant pinning mechanism in MgB$_2$.

References

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