Doped MgB$_2$ prepared by field assisted sintering technique

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Abstract. Field-assisted-sintering technique (FAST) has been employed to obtain polycrystalline MgB$_2$ samples, pristine and doped with 5 mol % SiC and B$_4$C, using commercial MgB$_2$ powder. The mass density of the samples is around 90% of the theoretical value. The response in magnetic field shows that the upper critical field and the irreversibility field are depressed by comparison with pristine MgB$_2$. The latter has an upper critical field $H_{c2} = 14.37$ T close to the values reported for the single crystals. Scaling analysis of the field dependence of the pinning force suggests that both addition of SiC and B$_4$C stabilizes two well defined pinning regimes in FAST-processed MgB$_2$. At low temperatures, $T < 24$ K ($H < 5$T), the pinning occurs at the grain boundaries whereas at higher temperatures there is a mixed pinning. These effects are supposed to be the combined result of relatively low level of C diffusion into the lattice of MgB$_2$, specific features in formation of the grain boundaries during FAST processing and the influence of the added materials on morphology. At high fields (above 8.5T) and 4.2K, doped samples are superior to the pristine one from the critical current density viewpoint.

1. Introduction

The new MgB$_2$ superconductor is currently considered a reliable choice for large scale applications of superconductivity in helium-free refrigerated systems. It displays intermediate characteristics between low and high temperature superconductors. This new physics is due to its unique two-band superconductivity. This outstanding characteristic makes possible the control of the upper critical field $H_{c2}$ by the doping-triggered interplay of the interband/intraband scatterings [1,2]. Substitutions, incorporation of nano-particles or irradiation substantially also enhance pinning force. The fabrication methods are as well important for the final characteristics of the samples.

A method to increase the density of the sample as well to reduce the processing time is to combine the uniaxial pressing with the application of a pulsed current. This procedure, which is known as field assisted sintering technique (FAST) makes possible to overcome the difficulties of consolidation of the samples [3, 4]. The field creates hot spots at the grain boundaries, possible local micro-plasmas enhancing the boundary (electro)diffusion and fasten the processes. Consequently, the MgB$_2$ samples obtained by FAST processing are more compact. At the same time the grain size

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usually does not increase [5, 6]. Additionally, the specific features of FAST may influence the pinning properties in a different manner than for the conventional processing technologies.

In this contribution, we report the results of our investigations concerning the properties of a series of polycrystalline MgB$_2$ samples, pure and added with SiC or B$_4$C, obtained by FAST.

2. Experimental and results

High grade raw materials, MgB$_2$, SiC, and B$_4$C have been used to obtain polycrystalline MgB$_2$ (MB), C-doped MgB$_2$ (MBBC), and SiC-doped MgB$_2$ (MBSC) with the ratio MgB$_2$/dopant equal to 95/5. Raw materials were mixed for 30 minutes in an agate mortar under argon atmosphere, put into a graphite dye, and placed in a “Dr. Sinter” spark plasma sintering system (Sumitomo Coal Mining Co). Working space was evacuated down to 15 Pa, and heated up with high intensity pulsed currents while applying a uniaxial pressure of 63 MPa. By this method, we succeeded to obtain samples with a density that is almost 90% the theoretical value (see Table 1).

The phase structure of the samples shows that B$_4$C does not influence the lattice parameters. Addition of SiC produces shrinkage of 20% of the a-axis keeping the c-axis constant. The use of SiC generates also traces of Mg$_2$Si (data not shown). The strongest effect of the dopants is the modification of the morphology of the samples (see figure 1). Specifically, B$_4$C generates large aggregates mixed with small particles (figure 1b). The sample doped with SiC displays a broad grain distribution with a lower connectivity (figure 1c).

![Figure 1. SEM micrographs of pristine and doped MgB$_2$ polycrystalline samples obtained by FAST (×4500).](image)

Magnetization $M$ vs temperature $T$ (SQUID, Quantum Design, 5T) data taken at 20 Oe applied field showed that the critical temperatures, which is 38.2 K in the case of the pristine MgB$_2$ sample, is reduced to 37.7 K and 37.9 K for MBBC and MBSC, respectively. This suggests an unexpected low degree of carbon substitution for boron [7, 8]. The upper critical field $H_{c2}$, as obtained from the similar measurements at different dc fields up to 7 T, follows the law $H_{c2}(T) = H_{c2}(0) \left[1 - \left(\frac{T}{T_c}\right)^2\right]^{\alpha}$ (solid symbols in figure 2). The fit of the data with this law shows that $H_{c2}(0) = 14.4$ T of the pristine sample is higher than the value previously reported for the FAST processed MgB$_2$ (8.5 T) [6]. The decrease of $H_{c2}$ for the doped samples seems to support a reduced carbon substitution for boron which probably requires much longer duration than the time used for preparation of the samples by this technique. To account for the substantial decrease of $H_{c2}$, we can invoke only the increased granularity of the doped
samples, which is noticeable in the micrographs (see figures 1b and 1a). Indeed, grainning increases the coherence length $\xi$ to $\xi_{\text{eff}} = \xi(2R+b)/t$, where $2R$ is the grain size, $t$ is the grain coupling length, and $b$ is the intergrain thickness [9] hence reduces the upper critical field to $H_{c2} = \Phi_0/2\pi\xi_{\text{eff}}^2$.

An estimate of the irreversibility field $H_{\text{irr}}$ was obtained as the zero of the Kramer plot $\Delta M^{1/2}H^{1/4}$ vs. $H$ [10], where $\Delta M$ is the half difference between the descending and ascending branches of the magnetization loop. $H_{\text{irr}}(T)$ obeys a similar law as $H_{c2}(T)$, $H_{\text{irr}}(T) = H_{\text{irr}}(0) \left[1 - \left(\frac{T}{T_c}\right)^{2\beta}\right]$ (empty symbols in figure 2). The pristine sample displays the classical exponent, $\beta \approx 3/2$ whereas the doped samples show an increased exponent $\beta \geq 1.75$ (See Table 1). At low temperatures, $T \leq 16$ K, doped samples show a higher irreversibility field than the pristine sample. This is confirmed by field dependence of the critical current density as extracted with the $1\mu$V/cm criterion from high field I-V characteristics measured at 4.2 K by the standard transport four-points method (see the inset to figure 2). Measurement were performed using a 15T JASTEC magnet installed at High Field Laboratory for Superconducting Materials, Tohoku University, Japan.

The sources of pinning which gives rise to the irreversible behaviour can be found out by a careful examination of the relationship between the reduced pinning force $f_p = \frac{F_p}{F_{p,\text{max}}}$, and the reduced field $h = \frac{H}{H_{\text{irr}}}$. Frequently, a scaling law of type $f_p = h^n(1-h)^m$ between the two quantities is expected. Therefore, we plotted $f_ph^n$ but the scaling for the pristine sample works when the variable is
while taking $1-h$ as variable works only for doped samples (figures 4a and 4b). These plots show a separation between high, $T > 20$ K, and low temperature behaviour as well as an important difference between pristine and doped samples. The pristine MgB$_2$ sample displays an exponential dependence that advocates for $f_p \propto h^n \exp(-Ah)$ with $n = 3$ for low temperatures and $n = 4$ for $T > 20$ K. Additionally, a change in the exponential factor $A$ is noticeable at high fields which we relate to the vanishing of the small $\pi$ gap. In the case of doped samples, the scaling is typical for pinning at the grain boundaries controlled by a shear process of flux line lattice, i.e., $f_p = h^{1/2}(1-h)^2$, at low temperatures whereas at higher $T$ the exponent $n$ is slightly higher, $f_p = h^{0.7}(1-h)^2$, suggesting an increased contribution of the pinning due to the point defects [11].

Table 1. Main characteristics of the MgB$_2$ samples prepared by FAST procedure

| Sample | Density (g/cm$^3$) | $T_c$ (K) | $H_{c2}(0)$ (T) | $\alpha$ | $H_{m}(0)$ (T) | $\beta$ |
|--------|-------------------|-----------|----------------|---------|----------------|--------|
| MB     | 2.39              | 38.2      | 14.4           | 1.21    | 7.93           | 1.48   |
| MBSC   | 2.37              | 37.7      | 8.6            | 1.16    | 8.24           | 1.86   |
| MBBC   | 2.08              | 37.9      | 9.2            | 1.07    | 8.43           | 1.75   |

Figure 3. Scaling relationship for the pristine MgB$_2$ sample. The lines are guides for the eye. A change in slope is noticeable at low temperatures and high fields.

Similar differences between doped and undoped samples were found out in the field dependence of the logarithmic derivative of the reversible magnetization $M_{rev}$. Actually, this derivative gives reliable information on the effective magnetic penetration depth, $\lambda^{-2} \propto \frac{dM}{d \ln H}$. In the case of the
pristine sample, $dM/d\ln H$, hence $\lambda^2_c$, decreases exponentially, $\lambda^2_c (H) = \lambda^2_c (0) \exp \left( -\frac{H}{H_0} \right)$ (figure 5a) while for the doped samples, $dM/d\ln H$, decreases as a power law $\lambda^2_c \propto H^{-\sigma}$ (figures 5b and 5c) and has a more reduced value. The decrease of $dM/d\ln H$ is expectable if we take into account the two-gapped nature of the superconductivity in MgB$_2$. The smaller $\Delta_2$ gap is fast suppressed by increasing field reducing the carrier density and, consequently, $\lambda^2_c \propto \frac{dM}{d\ln H}$. However, it is not clear why there is difference in the functional dependence. It is noteworthy that the pristine sample displays exponential decays both for the pinning force and for the penetration length.

Figure 4. Scaling relationship for the doped MgB$_2$ samples processed by FAST. a) C-doped MgB$_2$; b) SiC-doped MgB$_2$. The lines are guides for the eye.

Figure 5. Field dependence of the logarithmic derivative of the reversible magnetization for MgB$_2$ polycrystalline samples processed by FAST. a) pristine MgB$_2$; b) C-doped MgB$_2$; c) SiC-doped MgB$_2$. The lines are guides for the eye.
3. Conclusions

The properties of pristine and doped MgB$_2$ obtained by FAST are extremely sensitive to doping. In the case of the samples produced by FAST, C substitution for B is relatively low, but the influence of the doping material on the morphology, and hence on the pinning properties is significant. For the samples with addition of B$_4$C or SiC a mixed pinning state is observed from measurements in magnetic fields ($T > 24$K, $H \leq 5$T). The use of B$_4$C and SiC suppresses the upper critical field and the low field irreversibility when compared with the values for the pristine MgB$_2$ sample. The pristine sample reached an upper critical field close to the bulk values reported for single crystal. These values are higher than the values previously reported by other groups. At 4.2 K and high fields above 8.5T doped samples are better from the pinning characteristics viewpoint than the pristine sample. Doping also changes the field dependence of the logarithmic derivative of the reversible magnetization and the scaling law of the pinning force. The former can be connected to the effective penetration length, which in turn is related to the superconducting carrier density and the exponential decay could be attributed to the fast vanishing of the $\Delta_c$ gap when the field increases, leaving active only the $\Delta_0$ gap.

References

[1] Gurevich A 2003 Phys. Rev. B 67 184515
[2] Golubov A A and Koshelev A E 2003 Phys. Rev. B 68 104503
[3] Groza J R 1998 ASM Handbook Vol. 7: Powder Metal Technologies and Applications eds. P W Lee, W B Eisen and R M German (ASM International Handbook Committee: Ohio) pp. 583-589
[4] Aldica G, Badica P and Groza JR 2007 J. Optoelectron. Adv Mater. 9(6) 1742-1745
[5] Lee S Y, Yoo S Y, Kim Y W, Hwang N M and Kim D Y 2003 J. Am. Ceram. Soc. 86 1800
[6] Song K J, Park C, Kim S W, Ko R K, Ha H S, Kim H S, Oh S S, Kwon Y K, Moon S H, and Yoo S -I, 2005 Physica C 426-431 588
[7] Takenobu T, Ito T, Chi D H, Prassides K and Iwasa Y 2001 Phys. Rev. B 64 134513
[8] Mickelson W, Cumings J, Han W Q and Zettl A 2002 Phys. Rev. B 65 052505
[9] G. Deutschcr, O. Entin-Wohlman, and Y. Shapira Phys. Rev. B 22 4264 (1980)
[10] Kramer E J 1973 J. Appl. Phys. 44 1360
[11] Dew-Hughes D 1974 Philos. Mag. 30 293; Dew-Hughes D 1987 Philos. Mag. B 55 459

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