Improved superconducting properties in bulk MgB$_2$ prepared by high-energy milling of Mg and B powders

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Abstract

MgB$_2$ bulks were prepared by high-energy milling of Mg and B powders. The correlations between milling times, microstructure and superconducting properties were investigated in MgB$_2$ bulks. The samples were characterized by x-ray diffraction (XRD), energy dispersive spectrometry (EDX) and scanning electron microscopy (SEM), and the magnetization properties were examined with a superconducting quantum interference device (SQUID) magnetometer. The investigations showed that high-energy milling is an effective approach for obtaining fine crystalline (40–100 nm) bulk MgB$_2$ with good grain connectivity and high $J_c$ performance. The critical current density reaches $2.0 \times 10^6$ A cm$^{-2}$ at 15 K and 0.59 T, $5.7 \times 10^5$ A cm$^{-2}$ at 2 T and $3.0 \times 10^4$ A cm$^{-2}$ at 5 T.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The improvement of the intrinsic properties of MgB$_2$ was recognized as a decisive goal to enable potential applications [1]. Conventional powders and sintered polycrystalline bulk MgB$_2$ samples typically exhibit deteriorated superconducting properties due to weak pinning [2, 3]. Mechanically alloyed (MA) samples have grains about 1000 times smaller than hot deformed samples and samples sintered at high pressure [4]. The observed increased $H_{irr}(T)$ and high $J_c(H)$ manifest improved flux pinning of MA samples, which are attributed to the small grains and the enhanced number of grain boundaries in the nanocrystalline material [4]. It has been demonstrated before that the nanocrystalline sample has distinctly higher irreversibility fields than the bulk sample with micrometre-sized grains, especially at low temperature [5]. One possible reason for the strong pinning found for thin films as well is their small grain size, about 10 nm [5]. The mechanical alloying technique for MgB$_2$ powder preparation is expected to produce enhanced magnetic flux pinning by microstructure refinement. However, it takes as long as 20–100 h [4, 6–12] for in situ MA precursor powder preparation. We have investigated the possibility of using short-time unalloyed high-energy milling of Mg and B powders as the precursor material to prepare bulk MgB$_2$. It took only 5 h for the optimal samples for in situ powder preparation in this work. Samples prepared by this method presented fine grain sizes and showed high $J_c$ performance. The fact manifested itself that it is an efficient combination between conventional powder preparation and mechanical alloying techniques. The possible mechanisms of improved superconducting properties in MgB$_2$ superconductors prepared by high-energy milling of Mg and B powders are discussed in this paper.

Additionally, MgB$_2$ is a line compound [13] and a certain deviation of the stoichiometry leads to substantially increased critical current densities compared to the stoichiometric
composition [11]. Precursor powders with a Mg excess of 5% were employed in our experiment, with reference to the literature [11, 14–16].

2. Experimental details

Mg (99.8%) and amorphous B (95%) powders with 5% Mg surplus were placed under purified Ar atmosphere in an agate milling container and grinding balls. The milling was performed on a SPEX 8000M mill for different times ($t_m = 1, 5, 10$ h) using a ball-to-powder mass ratio of 3. The milled powders were then cold pressed to form pellets with a diameter of 20 mm and a height of 3 mm. The pellets were placed in an alumina crucible inside a tube furnace under ultra-high purity Ar atmosphere. The heat-treatment parameters were optimally chosen as $750^\circ$C and 1 h from our previous work [17]. The samples were then cooled down to room temperature.

The phase compositions of the samples were characterized with an APD1700 x-ray diffractometer. The surface morphologies and microstructures of the samples were characterized by JSM-6460 and JSM-6700F scanning electron microscopes.

A SQUID magnetometer (Quantum Design) was used to measure the AC magnetic susceptibility of the samples over a temperature range from 5 to 50 K under an applied field of 1 Oe. Magnetization versus magnetic field ($M$–$H$) curves were also measured on rectangular-shaped samples at temperatures of 10 and 15 K under magnetic fields up to 90 000 Oe to determine the critical current density $J_c(H)$.

3. Results and discussion

XRD and EDX analyses reveal the appearance of a small amount of MgO impurity for both as-milled and sintered samples. The relative percentage composition of MgO phase is gradually increased with prolonged milling time for both samples. This is most probably because of the oxide diffusing into the grain surfaces during the particle reduction process and unavoidable oxygen traces during the sintering process.

The microstructures of the investigated samples are shown in figure 1. Scanning electron microscope images mainly show spherical grains of about 40–100 nm in size for the 5 h milled sample. The impurity phases are evidently observed for the sample milled for 10 h, as marked by black arrows. Figure 2 indicates the distribution of the second phases for differently milled bulk MgB$_2$. There are a few small dark grey impurity phases for the sample milled for 1 h. The sample milled for 5 h has few impurity phases. However, there are a large number of stripped impurity phases for the sample milled for 10 h.

The magnetic field dependence of magnetization for samples milled for different times is shown in figure 3. $J_c(H)$ was calculated by the Bean critical state model from the magnetization curves (see figure 4). The irreversible field is shown in the inset as a function of milling time. $H_{irr}$ values were determined from the closure of hysteresis loops with a criterion of $J_c = 10^2$ A cm$^{-2}$ [18]. As we can see, the sample milled for 5 h has a significantly higher $H_{irr}$ and $J_c$ than the other samples in the magnetic field. The critical
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Figure 4. Magnetization critical current density $J_c$ as a function of magnetic field $H$ at 15 K for samples heated at 750 °C and milled for different times. Inset: the irreversible field as a function of milling time. The $H_{irr}$ values were determined from the closure of hysteresis loops with a criterion of $J_c = 10^5$ A cm$^{-2}$ [18].

Figure 5. Field dependence of the volume pinning force $F_p(H)$ at 15 K for samples heated at 750 °C and milled for different times. $F_p(H)$ is normalized by the maximum volume pinning force $F_{p,max}$ at the same temperature and for different milling times.

Current densities reach $2.0 \times 10^6$ A cm$^{-2}$ at 15 K and 0.59 T, $5.7 \times 10^5$ A cm$^{-2}$ at 2 T and $3.0 \times 10^5$ A cm$^{-2}$ at 5 T. The improved pinning of this material seems to be caused by enhanced grain boundary pinning provided by the large number of grain boundaries in the sample.

The maximum $J_c$ was not initially discovered in our MgB$_2$ bulks with ball-milled precursor powders. Flukiger et al [19] declared that $J_c$ of ex situ Fe/MgB$_2$ tapes with ball-milled powders first shows an enhancement for particle sizes of 3/30 μm, which are the two peak values in the size distribution obtained by granulometry, followed by a decrease for further reduction of particle sizes with distribution peaks 1.5/10 μm and distribution peak 1 μm. They thought that the maximum of $J_c$ is a compromise between enhanced flux pinning at the grain boundaries, caused by these chemical impurities at the nanoscale, and a decrease of $J_c$, caused by the introduction of too many impurities, reducing the percolation of the current. However, Perner et al [10] considered that there are two competing processes taking place during the high-energy milling. The first one initiates an improvement of the superconducting properties of bulk MgB$_2$. It is attributed to the grain refinement resulting in a higher reactivity and, therefore, an optimal grain connectivity and high density of grain boundaries in MgB$_2$ bulks. The second process is expected to be the introduction of oxygen from the working atmosphere with increasing milling time, causing increased content of impurity phases with a reduced grain connectivity. Both analyses are reasonable. However, the mechanism underlined for the effect of the reduction of MgB$_2$ particle size by ball milling on the improvement of $J_c$ are still controversial. Carmine Senatore et al [20] have investigated the third harmonic response of the AC susceptibility as a function of the DC magnetic field up to 9 T, at different temperatures, for various frequencies and amplitudes of the AC field. From their point of view, the transport properties of Fe/MgB$_2$ tapes with ball-milled powders are determined by both the strength of pinning centres and the connectivity of the grains. There are two well separated peaks in the curves of magnetic field dependence of the third harmonic modulus $|\chi_3|_c(B)$. The low-field peak is determined by intergranular currents. The high-field peak corresponds to the currents flowing inside the grains. The ball-milling process, which reduces the size of the powder grains, leads to an improvement of the connectivity which is confirmed by the disappearance of the intragrain peak after 3 h and 100 h ball milling of the powders used for the tapes. The Fe/MgB$_2$ tapes with ball-milled powders also exhibit an increase of the peak amplitude of the third harmonic modulus with frequency. This increase was attributed to the fact that the pinning mechanism is not changed by ball milling of the initial powder, whereas the strengths of the pinning centres are increased as a consequence of the increased total surface area of the powder grains. Scaling of the $F_p(B)$ curves at different temperatures shows that the pinning centres are confined to the grain boundaries.

Figure 5 shows the field dependence of the volume pinning force $F_p(H)$ at 15 K for samples heated at 750 °C and milled for different times. $F_p(H)$ is normalized by the maximum volume pinning force $F_{p,max}$ at the same temperature and for different milling times. The shapes of these profiles depend on the milling time. For the 5 h milled sample, the $F_p(H)/F_{p,max}$ values were obviously larger than those of other samples over 1 T, indicating enhanced flux pinning in high-field region. The $F_{p,max}$ values of the 1 and 5 h milled samples reach 11.3 and 13.4 GN m$^{-3}$ at 15 K. These values are nearly in the range of commercial superconductors, NbTi and Nb$_3$Sn, which show 15–30 GN m$^{-3}$ at 4.2 K [21].

Figure 6 shows a comparison of magnetic $J_c(H)$ for a 5 h milled sample with data reported in the literature [22–25]. $J_c$ for this sample exhibits a better field performance and higher values of $J_c$. In a magnetic field lower than 3.5 T, our 5 h milled sample shows the highest $J_c$ at 15 K. The best $J_c$ for the 5 h milled sample was $2.3 \times 10^6$ A cm$^{-2}$ at 3 T and 15 K, which exceeds the $J_c$ values of state-of-the-art Ag/Bi-2223 tapes. Our 5 h milled MgB$_2$ sample is even comparable with SiC-doped MgB$_2$ bulks made by Dou’s group [24], which had exhibited the strongest reported flux pinning and the highest $J_c$ in high fields to date.
In conclusion, we have succeeded in preparing high critical current density bulk MgB$_2$ by the high-energy ball-milling technique. It is demonstrated that this is an effective approach for obtaining fine crystalline bulk MgB$_2$ with good grain connectivity and extraordinary high $J_c$ performance. The flux pinning is enhanced in our sample by a large number of grain boundaries. Further improvement is expected to be obtained in doped samples using the high-energy ball-milling technique.

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References

[1] Larbalestier D C et al 2001 Nature 410 186–9
[2] Bugoslavsky Y, Perkins G K, Qi X, Cohen L F and Caplin A D 2001 Nature 410 563–5
[3] Bugoslavsky Y, Cohen L F, Perkins G K, Polichetti M, Tate T J, Gwilliam R and Caplin A D 2001 Nature 411 561–3
[4] Narozhnyi V N et al 2002 SCRM2002: Int. Conf. on Superconductivity, CMR & Related Materials: Novel Trends (Giens, France, June 2002)
[5] Fuchs G, Muller K-H, Handstein A, Nenkov K, Narozhnyi V N, Eckert D, Wolf M and Schultz L 2001 Solid State Comun. 118 497–501
[6] Gumbel A, Perner O, Eckert J, Fuchs G, Nenkov K, Muller K-H and Schultz L 2003 IEEE Trans. Appl. Supercond. 13 (2) 3064–7
[7] Gumbel A, Eckert J, Fuchs G, Nenkov K, Muller K-H and Schultz L 2002 Appl. Phys. Lett. 80 2725–7
[8] Halter W, Roding C, Fischer C, Holzapfel B, Perner O, Eckert J, Nenkov K and Fuchs G 2003 Supercond. Sci. Technol. 16 281–4
[9] Fischer C, Roding C, Halter W, Perner O, Eckert J, Nenkov K, Fuchs G, Wendrock H, Holzapfel B and Schultz L 2003 Appl. Phys. Lett. 83 1803–5
[10] Perner O, Eckert J, Halter W, Fischer C, Muller K-H, Fuchs G, Holzapfel B and Schultz L 2004 Supercond. Sci. Technol. 17 1148–53
[11] Perner O, Halter W, Fischer C, Fuchs G, Holzapfel B, Schultz L and Eckert J 2005 IEEE Trans. Appl. Supercond. 15 (2) 3192–5
[12] Perner O, Eckert J, Halter W, Fischer C, Acker J, Gennning T, Fuchs G, Holzapfel B and Schultz L 2005 J. Appl. Phys. 97 056105
[13] Massalski T (ed) 1990 Binary Alloy Phase Diagrams 2nd edn (Materials Park, OH: ASM International)
[14] Serquis A, Civale L, Coulter J Y, Hammon D L, Liao X Z, Zhu Y T, Peterson D E, Mueller F M, Nesterenko V F and Indrakanti S S 2004 Preprint cond-mat/0404052
[15] Zhou S, Pan A V, Liu H and Dou S 2002 Physica C 382 349–54
[16] Fang H, Gijavanekar P, Zhou Y X, Liang G, Putman P T and Salama K 2005 IEEE Trans. Appl. Supercond. 15 (2) 3200–3
[17] Wu Y et al 2006 Preprint cond-mat/0603536
[18] Zhao Y, Cheng C H, Feng Y, Machi T, Huang D X, Zhou L, Koshizuka N and Murakami M 2003 Physica C 386 581–7
[19] Flukiger R, Suo H L, Musolino N, Beneduce C, Toulemonde P and Lezza P 2003 Physica C 385 286–305
[20] Senatore C, Clayton N, Lezza P, Pace S and Flukiger R 2005 IEEE Trans. Appl. Supercond. 15 (2) 3239–332
[21] Fuji H, Togano K and Kumakura H 2003 Supercond. Sci. Technol. 16 432–6
[22] Senkowicz B J, Giencke J E, Patnaik S, Eom C B, Hellstrom E B and Larbalestier D C 2004 Preprint cond-mat/0411199
[23] Perner O, Eckert J, Halter W, Fischer C, Acker J, Gennning T, Fuchs G, Holzapfel B and Schultz L 2005 J. Appl. Phys. 97 056105
[24] Dou S X, Soltanian S, Horvat J, Wang X L, Zhou S H, Ionescu M and Liu H K 2002 Appl. Phys. Lett. 81 3419–21
[25] Soltanian S, Horvat J, Wang X L, Munroe P and Dou S X 2003 Physica C 390 185–90