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Abstract

MgB₂ superconductors with unique microstructures were rapidly fabricated at low temperatures, and exhibited significantly improved critical current density (J_c). According to the microstructure observations, the prepared samples consisted of lamellar nano MgB₂ grains with many embedded nanoimpurities (about 10 nm). The formation of these lamellar nano MgB₂ grains is associated with the presence of a local Mg-Cu liquid at sintering temperatures as low as 575°C. The ball milling treatment of the original powders also plays a positive role in the growth of lamellar grains. Based on an analysis of the relationship between resistivity and temperature, the lamellar nano MgB₂ grains in the prepared sample possess better grain connectivity than the typical morphology of MgB₂ samples prepared by traditional high-temperature sintering. Furthermore, the presence of many nano MgB₂ grain boundaries and nano impurities in the prepared sample can obviously increase the flux pinning centers in accordance with the analysis of flux pinning behavior. Both factors mentioned above contribute to the significant improvement in J_c from low field to relative high field. The method developed in the present work is an effective and low-cost way to further enhance J_c in MgB₂ superconductors across a wide range of applied magnetic fields without using expensive nanometer-sized dopants. The Royal Society of Chemistry 2012.

Keywords

mgb₂, grains, flux, pinning, centers, nanoimpurities, their, synthesis, significantly, improved, critical, current, density, nano, lamellar

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PAPER

The synthesis of lamellar nano MgB₂ grains with nanoimpurities, flux pinning centers and their significantly improved critical current density

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MgB₂ superconductors with unique microstructures were rapidly fabricated at low temperatures, and exhibited significantly improved critical current density (J_c). According to the microstructure observations, the prepared samples consisted of lamellar nano MgB₂ grains with many embedded nanoimpurities (about 10 nm). The formation of these lamellar nano MgB₂ grains is associated with the presence of a local Mg–Cu liquid at sintering temperatures as low as 575 °C. The ball milling treatment of the original powders also plays a positive role in the growth of lamellar grains. Based on an analysis of the relationship between resistivity and temperature, the lamellar nano MgB₂ grains in the prepared sample possess better grain connectivity than the typical morphology of MgB₂ samples prepared by traditional high-temperature sintering. Furthermore, the presence of many nano MgB₂ grain boundaries and nano impurities in the prepared sample can obviously increase the flux pinning centers in accordance with the analysis of flux pinning behavior. Both factors mentioned above contribute to the significant improvement in J_c from low field to relative high field. The method developed in the present work is an effective and low-cost way to further enhance J_c in MgB₂ superconductors across a wide range of applied magnetic fields without using expensive nanometer-sized dopants.

1. Introduction

The superconductivity at 39 K discovered in MgB₂, a chemical of simple binary composition, has attracted much interest in techniques for its fabrication and practical application.^{1,2} However, the critical current density in MgB₂ is still small compared to expectations for an optimized material. Flux pinning and grain connectivity are the critical factors determining the performance of J_c in type II superconductors. In order to obtain practical MgB₂ superconductors, a variety of processing techniques have been investigated to improve J_c in MgB₂ superconductors, including irradiation,^{3,4} chemical doping^{5–11} and ball milling.^{12–15} Among them, nano SiC doping has proved to be the most effective way of improving J_c , especially at high fields.^{6,8} In general, the techniques mentioned above have focused on enhancing flux pinning by engineering grain boundaries or introducing nano-impurities and lattice defects, but have tended to neglect and even impair the associated issues of connectivity, which limits further improvements in J_c .¹⁶ As a result, it makes sense to develop an effective way of both improving the grain connectivity of MgB₂ and increasing flux pinning centers with the specific aim of further enhancing J_c .²

According to the theory of type II superconductors, grain connectivity and flux pinning in MgB₂ are both closely related to the micro-morphology of MgB₂ grains. Thus optimizing the morphology of MgB₂ grains by means of developing new manufacturing techniques is a possible approach for further improving J_c .

In the present work, MgB₂ samples with unique microstructures, *i.e.*, lamellar nano MgB₂ grains containing many homogeneously embedded nanoimpurities, were rapidly synthesized by ball milling and subsequent Cu-activated sintering at low temperature. They were shown to exhibit significantly improved J_c . In particular, the value of J_c in the prepared MgB₂ sample was more than 1×10^5 A cm^{−2} at 2 T, 20 K, which is much higher than that of typical pure and nano SiC doped MgB₂ sample sintered at high temperature and basically meets the need of practical applications at this field.

2. Experimental

Mg powder (99.8% purity, 100 μm in size), amorphous B powder (99% purity, 25 μm in size) and Cu powder (99.9% purity, 3 μm in size) were mixed in a molar ratio of (MgB₂)_{0.97}Cu_{0.03}. Then tungsten carbide milling balls and the mixed powder were put into a tungsten carbide vessel with a ball-to-powder-weight-ratio of 5 : 1 in an argon box. High energy ball milling was performed on a SPEX 8000M mill under an argon atmosphere. The powders after milling for 5 h and 10 h were characterized by X-ray diffraction (XRD) in the Bruker D8 Advance X-ray

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diffractometer, respectively. Then the milled powder was pressed into a flake under a pressure of 5 MPa and sintered at 575 °C for 5 h under high purity flowing argon (99.99%, $O_2 < 10$ PPM). The phase evolution during the sintering process was detected by an *in situ* X-ray diffractometer. As a reference, an undoped MgB_2 sample without milling was also prepared by traditional sintering at 850 °C for 0.5 h under high purity flowing argon. Then the microstructure of all the sintered samples was observed using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM). The temperature dependence of resistivity in the sintered samples was investigated by a DC four-probe method. Finally, the magnetization of the sintered samples was measured using a physical property measurement system. Then the J_c was calculated from the width of the magnetization hysteresis loops (ΔM) based on the extended Bean model.

3. Results and discussion

Fig. 1 shows the XRD pattern of the original $Mg + B$ mixed powder and $Mg + B + 3\%$ Cu powder after milling for different times. It can be seen that Mg is the main phase in the original and the milled powder. As milling time increases, the intensity of the Mg peaks gradually decreases and their corresponding widths broaden, which is mainly attributed to grain refinement and accumulation of micro-strain resulting from ball milling. During ball milling, it is very easy for Mg to be oxidized.^{14,15} The suppression of powder oxidation should be considered when the ball milling technique is applied. In the present work, no obvious oxide peaks (MgO , CuO or B_2O_3) are observed, as shown in Fig. 1. This means that the oxidation of powder is well suppressed during the milling process due to the argon protection.

Fig. 2 illustrates the *in situ* phase evolution during sintering of the original and milled powder at 575 °C. In the *in situ* XRD pattern of the reference sample without milling or addition of Cu, a lot of residual Mg peaks can be recognized, which implies that the reaction between Mg and B is not complete even after sintering for 5 h (see Fig. 2a). This result is consistent with previous studies.^{17,18} Actually, the reaction between Mg and B at low

Fig. 1 The XRD pattern of original $Mg + B$ mixed powder and $Mg + B + 3\%$ Cu powder after milling for different times.

Fig. 2 The *in situ* phase evolution during the sintering of the original and milled powders at 575 °C with (a) original powder, (b) 5 h-milled $Mg + B + 3\%$ Cu powder and (c) 10 h-milled $Mg + B + 3\%$ Cu powder.

temperatures takes a very long time to form a complete MgB_2 phase as a result of the low diffusion rate of atoms in the solid state below the melting point of Mg.^{18,19} On the other hand, the formation of a complete MgB_2 phase is almost complete in the

milled MgB_2 sample by Cu-activated sintering for only 2 h. In our previous studies, the addition of Cu was reported to accelerate the formation of the MgB_2 phase during low-temperature sintering by the presence of a local Mg–Cu liquid.¹⁹ The broad diffuse and smooth peak that appears between 35° and 40° in the *in situ* XRD patterns of Cu-doped samples after sintering for 1 h and 2 h (see Fig. 2b and 2c) confirms this opinion. It is worth noting that ball milling treatment can further improve the efficiency of Cu activated sintering of MgB_2 at low temperatures. Thus, the reaction between Mg and B is finished after Cu activated sintering for only 2 h in the milled MgB_2 samples. Look at Fig. 2 more carefully, the phase evolution undergoes different routes during the *in situ* Cu activated sintering process for the samples milled for 5 h and 10 h, especially after sintering for 2 h. For 5 h-milled sample, after sintering for 2 h, there is no obvious change in the phase composition. But in the 10 h-milled sample, the intensity of both MgO peaks and MgCu_2 peaks are gradually increased as sintering time increasing from 2 h to 5 h. This result implies that after milling for 10 h the Mg particles become more active, and during the subsequent sintering process they can more easily react with residual O in the protected argon gas and Cu, forming more MgO and MgCu_2 , respectively.

Whether these impurities such as MgO and MgCu_2 can serve as flux pinning centers mainly depends on their size and microstructure distribution in the MgB_2 matrix. Fig. 3 shows SEM images of sintered samples. It was observed that the MgB_2 grains in the milled MgB_2 samples prepared by Cu-activated sintering at low temperature were much smaller and less regular than those in the reference MgB_2 sample prepared by sintering at high temperature (see Fig. 3a, 3b, and 3c).² Moreover, in the milled samples, the MgB_2 grains contact each other tightly with fewer voids distributed within them and it is difficult to recognize single regular MgB_2 grains among these MgB_2 grains. These results are mainly attributed to the milling treatment of original powder and the suppression of volatilization of Mg during the low-temperature sintering process. In the 10 h-milled sample sintered at low temperature, there are many nanoimpurities (the white dots marked by black arrows with size of about 5–10 nm, see Fig. 3c) embedded within the MgB_2 grains. This is quite different from the microstructure of the reference and 5 h-milled samples. Combined with the *in situ* XRD results (see Fig. 2c), these nanoimpurities can be identified as MgO or MgCu_2 . The size of these nanoimpurities is comparable to the coherence length of MgB_2 and thus could serve as flux pinning centers. After observing Fig. 3c carefully, small MgB_2 grains (about 50–100 nm) found to arrange in ordered and lamellar grains can be recognized unexpectedly (see the typical regions marked by white squares in Fig. 3c).

The microstructure of these lamellar nano grains was further investigated by HRTEM in detail and the corresponding images are shown in Fig. 4. It can be seen from Fig. 4a that the MgB_2 matrix has an obvious layered structure. The planar distance of the lamellar MgB_2 matrix is 0.213 nm (see Fig. 4b), which corresponds to $[101]_{\text{MgB}_2}$, the theoretical first preferentially growing crystal plane of MgB_2 during sintering. The formation of these lamellar nano grains should be associated with the presence of local Mg–Cu liquid at sintering temperatures as low as 575°C . Obviously, it is easier for MgB_2 grains to grow in the preferentially growing crystal plane following the direction of

Fig. 3 SEM images of sintered samples with (a) reference MgB_2 sample sintered at high temperature, (b) 5 h-milled MgB_2 sample fabricated by Cu activated sintering at low temperature and (c) 10 h-milled MgB_2 sample fabricated by Cu activated sintering at low temperature.

local Mg–Cu liquid than other directions without Mg–Cu liquid. Besides, the ball milling treatment can further improve Cu activated sintering efficiency of MgB_2 as well as refine the MgB_2 grains. As a result, lamellar nano MgB_2 grains are formed at a low sintering temperature. One can also recognize that there is a nanoparticle with a diameter of about 8 nm embedded in the lamellar MgB_2 matrix, marked by a white arrow in Fig. 4b. This result is consistent with the SEM image in Fig. 3c, which both confirm the existence of nanoimpurities that can serve as flux pinning centers.

Based on the above microstructure observations, the morphology of the milled sample prepared by Cu activated sintering at low temperature is quite different from the typical morphology of the reference standard MgB_2 sample prepared by

Fig. 4 The HRTEM image of lamellar nano MgB₂ grains in the 10 h-milled MgB₂ sample fabricated by Cu activated sintering at low temperature.

sintering at high temperature. This unique morphology should significantly influence the performance of J_c .

Measured J_c - H characteristics of the reference MgB₂ prepared by sintering at high temperature and milled samples prepared by

Fig. 5 At 20 K, measured J_c - H characteristics of the reference MgB₂ prepared by sintering at high temperature and milled samples prepared by Cu activated sintering at low temperature.

Cu activated sintering at low temperature are shown in Fig. 5. Besides, the J_c - H curve of nano SiC-doped samples was also given in Fig. 5.²⁰ It was found that milled MgB₂ samples prepared by Cu activated sintering at low temperature exhibit an excellent J_c that is much higher than that of the reference MgB₂ sample sintered at high temperature. At self-field and low fields (below 2.5 T), the 10 h-milled samples are much higher than that of the reference and SiC-doped MgB₂ samples sintered at high temperature (see Fig. 5).^{6,10,20} This is superior to the results obtained from SiC-doped samples sintered at high temperature, which generally underwent notable degradation in the J_c at low fields compared to pure MgB₂ samples.^{6,10,21} In previous studies,^{19,22,23} minor Cu doping was found to enhance J_c of MgB₂ superconductors at low fields. Compared to these Cu doped MgB₂ samples prepared by sintering at low temperature and high temperature,^{19,22,23} the 10 h-milled sample prepared by Cu activated sintering at low temperature in the present work still possesses higher J_c at low fields. This result should be related to the higher density and the presence of lamellar MgB₂ grains in the 10 h-milled sample (see Fig. 3c and Fig. 4), which could effectively improve the grain connectivity of MgB₂. Hereby, in order to investigate the grain connectivity of prepared samples in the present work, the temperature dependence of resistivity in the sintered samples was measured and the results are given in Fig. 6.

Both the 10 h-milled sample and the reference sample prepared in the present work exhibit high T_c (38 K), which is comparable to that of standard MgB₂ bulk¹ (see Fig. 6). According to the Rowell connectivity analysis, the calculated active cross-sectional area fraction (A_F) represents the connectivity factor between adjacent grains.^{16,24} Here the A_F is estimated as:

$$A_F = \Delta\rho_{\text{ideal}}/(\rho_{300\text{ K}} - \rho_{40\text{ K}}) \quad (1)$$

$$\Delta\rho_{\text{ideal}} = \rho_{\text{ideal}}(300\text{ K}) - \rho_{\text{ideal}}(40\text{ K}) \quad (2)$$

Where ρ_{ideal} is the resistivity of a reference crystal and ρ_T is our measured resistivity at temperature T . here the $\Delta\rho_{\text{ideal}}$ is 7.3 $\mu\Omega$ cm, according to previous study.^{16,21}

Fig. 6 The temperature dependence of resistivity of the reference MgB₂ prepared by sintering at high temperature and 10 h-milled samples prepared by Cu activated sintering at low temperature.

Accordingly, the calculated A_F is about 0.30 and 0.20 for 10 h-milled sample and reference MgB_2 sample, respectively. This result indicates that the 10 h-milled MgB_2 sample fabricated by Cu activated sintering possesses much better grain connectivity than the reference MgB_2 sample fabricated by traditional sintering. Hence, it is not difficult to explain why the J_c of 10 h-milled MgB_2 sample fabricated by Cu activated sintering is much higher than that of the reference MgB_2 sample. Since the 10 h-milled MgB_2 sample contains many more impurities (MgO and MgCu_2) that could depress the grain connectivity of MgB_2 than the reference MgB_2 sample,¹² and it was previously reported that ball milling treatment of original powders could obviously decrease the grain connectivity of the final sintered MgB_2 sample,¹⁶ the grain connectivity of 10 h-milled MgB_2 sample ought to have been worse than that of the reference MgB_2 sample. From this view, the abnormal-but-excellent grain connectivity of the 10 h-milled sample in the present work must be mainly attributed to the presence of lamellar nano MgB_2 grains and higher sintering density.

Looking back at Fig. 5, at middle and relatively high fields (from 2.5 T to 3.5 T), the level of enhancement in J_c of 10 h-milled samples is even higher than that of SiC-doped samples sintered at high temperature.²⁰ This can be mainly attributed to the presence of lots of nano MgB_2 grain boundary pinning centers and nano impurity pinning centers in this sample (see Fig. 3c). In addition, as mentioned above, the excellent grain connectivity in this sample has also contributed to the improved J_c at middle and high fields.

Further analysis of flux pinning behavior in terms of the flux pinning force provides us with deeper insights. Fig. 7 shows the normalized pinning force $F_p/F_{p\max}$ as a function of a reduced magnetic field h in the prepared samples with $h = H/H_{\text{irr}}$. The irreversibility field (H_{irr}) has been estimated by extrapolating the $J_c^{1/2}H^{1/4}$ vs. H curve to the horizontal axis, also called the Krammer extrapolation. Flux pinning curves for the 10 h-milled samples prepared by Cu activated sintering at low temperature are shifted to the right compared to the reference

MgB_2 sample. The clear shift of the peak of the pinning force curve towards higher field reveals the additional pinning centers in this sample besides grain boundary pinning. As described earlier, MgO and MgCu_2 nanoimpurities with a size comparable to the coherence length of MgB_2 can act as pinning centers, which is the main reason for the shift in the $F_p/F_{p\max}$ vs. H curve towards higher field. It can be also seen from Fig. 7 that for the 10 h-milled sample the peak is broader than the reference sample, indicating a higher pinning strength is for this sample; this is confirmation of the J_c result. In the present case it is seemingly the combination of grain boundary pinning and nanoimpurity pinning.

4. Conclusions

MgB_2 samples consisting of lamellar nano MgB_2 grains containing many dispersed nanoimpurities were prepared by a ball milling treatment of the original powder and subsequent Cu activated sintering at a low temperature. The higher sintering density and lamellar MgB_2 grains in the present sample exhibit better grain connectivity than the typical morphology of MgB_2 samples prepared by the traditional high-temperature sintering. Additionally, lots of nano MgB_2 grain boundaries and nano impurities in the prepared sample can obviously increase flux pinning centers. Both of these factors contribute to the significant improvement in J_c from low field to relative high field. From this point of view, the method developed here is an effective way of both improving the grain connectivity of MgB_2 and increasing flux pinning centers. Hence, it is also a promising and low-cost way to further improve the J_c of MgB_2 superconductors across the entire applied magnetic range without using expensive nanometer-sized dopants.

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Fig. 7 The normalized pinning force $F_p/F_{p\max}$ as a function of reduced magnetic field h in the reference MgB_2 sample prepared by sintering at high temperature and 10 h-milled samples prepared by Cu activated sintering at low temperature with $h = H/H_{\text{irr}}$.

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