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RESEARCH ARTICLE

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High-density MgB_2 superconducting bulk samples prepared at ambient pressure

Abstract High-density MgB_2 (HD-MgB_2) superconducting samples ($D \geqslant 2.2$ g/cm^3), using different sources of magnesium powder as raw material, were synthesized in ambient pressure in a rich Mg environment. The magnesium powders used in the fabrication process include nanometer-sized magnesium particles, powders from Alfa Aesar, ordinary off-the-shelf powder, and magnesium chip. The fabrication procedure involved a double-sintering process in a rich-Mg environment. A transition temperature T_c of 39 K was observed. Samples with the equally high density and matching superconducting properties were obtained as well by a triple sintering process of the MgB_2 powder directly from Alfa Aesar.

Keywords high-density MgB_2 superconductor, magnesium vapor in all directions, sintering process

PACS numbers 74.70.Ad, 74.25.Ha, 74.62.Yb, 74.62.Bf

1 Introduction

The long existing binary compound, MgB_2, has been found to be superconducting [1] in 2001. This discovery led to a whole new class of superconducting materials beyond the existing metallic, organic, molecular, and high T_c oxide superconductors. This discovery had a huge impact in the field of superconductivity and generated both experimental and theoretical interest in research, focusing on this specific material and on the related boron compounds (see the review article [2] and the references therein).

Various fabrication techniques have been applied to prepare different forms of MgB_2, including bulk, thin film, thick film, wires, tapes, powders, and single crystal. The properties of the resulting material depend on the fabrication methods and the raw materials. The previous investigations show that the density of the sample is a key factor to superconducting properties. The higher the density is, the better the performance will be. For the sample prepared in vacuum or in argon environment for single-sintering process, the density usually does not exceed 1.6 g/cm^3, which is 63 % of the theoretical value of , 2.55 g/cm^3 [2]. On the other hand, HD-MgB_2 usually is fabricated in high-pressure environment at high temperature. The sample thus prepared has a T_c decreasing at a large rate of−1.11 to −1.6 K/GPa [2,3]. We report a new technique of producing polycrystalline MgB_2 with a high density of ~ 2.2 g/cm^3 . This method is simple and cost-effective than the high pressure–high temperature method.

2 Sample fabrication

It is usually difficult to obtain HD-MgB_2 sample by a process at ambient pressure as magnesium diffuses easily out of the sample during the sintering process at high temperature, resulting in the formation of numerous cavities. This reduces the sample density. The size of the cavities depends on the grain size of the magnesium raw materials. Hence the sample density varies. In order to raise the sample density to improve superconducting properties, a double sintering process at ambient pressure was developed. The second sintering process was performed on the ground MgB_2 powder obtained from the initial sintering process using magnesium

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and boron as the raw material. The main idea is to supply magnesium constantly to supplement loss due to diffusion in the secondary sintering process. Figure 1 depicts a simple diagram of magnesium in and out of the sample during the sintering. The letter “A” represents a piece of MgB_2 sample under second process with an adequate volume of magnesium source “B” placed by the side. The rate of magnesium diffusing out of the sample, d_1, is roughly equal from every side of the sample, while those into the sample vary in the order $d_2'' < d_2' < d_2$. In order to produce samples of HD-MgB_2 with higher concentration of magnesium, the condition, $d_2'' \geqslant d_1$, is necessary.

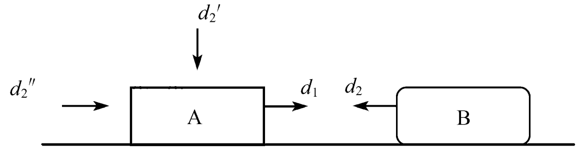

Fig. 1 Simulated picture for the magnesium out off and diffused into re-sintering MgB_2 superconductor sample. **A**: a piece of re-sintering MgB_2 superconductor sample; **B**: extra magnesium source.

In the present work, a method to fabricate HD-MgB_2 sample in ambient pressure is reported. The sample is surrounded by magnesium vapor during the initial sintering and the second re-sintering processes. Three boxes were prepared for that purpose. Two were made of tantalum foils (0.15 mm in thickness), denoted as box 1 (3.5 × 2.2 × 1.2 cm^3) and box 2 (5.0 × 3.0 × 2.0 cm^3). The third one, referred to as box 3 (inner size is 2.5 × 1.0 × 0.80 cm^3), is made of six pieces of magnesium-enriched MgB_2 bulk samples with the addition of 30 wt% of ordinary off-the-shelf magnesium powder.

The polycrystalline MgB_2 samples were prepared by solid-state reaction method. Four MgB_2 samples were produced using different magnesium powders as raw materials reacting with boron. The raw material magnesium includes magnesium particles in nanometer size ($\geqslant$ 40 nm) (sample 1), magnesium chips of about 2-mm length (sample 2), powders from Alfa Aesar with 380 mesh (sample 3), and ordinary off-the-shelf magnesium powder with grain size $\leqslant$ 0.2 mm (sample 4). They were mixed very well with boron powder (99.999 % pure and grain size of $\approx$ 1 μm) in a stoichiometric ratio of 1 : 2 Mg : B, then pressed into rectangular embryo of 2.5 × 0.60 × 0.20 cm^3. The treatment of the Alfa Aesar MgB_2 powder (for sample 5) was also carried out using a sample of the same size. A pressure of 670 MPa was applied. The MgB_2 embryo sample was put into box 3, which was then placed into box 1. After this, box 1 was put into box 2. Box 2 was then sintered inside a quartz tube with high-purity argon environment at a furnace temperature of 750°C for 2 hours. The temperature of the furnace increased from room temperature to 750°C in 2 hours at a fixed rate. The furnace was allowed to cool in ambient air. After the initial sintering process, the sample volume expanded. These five samples were reground and pressed, then put into rectangular boxes again with a pressure of 860 MPa. The subsequent process of the heat treatment was the same as in the initial process except that the furnace temperature was increased to 770°C. For the re-sintering process, the building blocks of the box 3 were refreshed with the magnesium-enriching process in order to ensure magnesium concentration. The density of the MgB_2 samples produced by the process described above was greater than or equal to 2.2 g/cm^3.

3 Measurement and results

Powder X-ray diffraction (XRD) pattern was generated by a Philip x’ pert diffractometer to investigate the structure. The spectrum is shown in Fig. 2. All of the five samples display hexagonal MgB_2 phase with traces of Mg and MgO phases. The Mg phase was due to the excessive magnesium that diffuses into and accumulates in the sample. The existence of MgO was attributed to the original Mg raw material used or to the reaction of Mg with the adsorbed oxygen during heat treatment. The deduced lattice parameters, along with the sample density, are listed in Table 1. As comparison, the crystal parameters from previous works of other groups are listed in the same table.

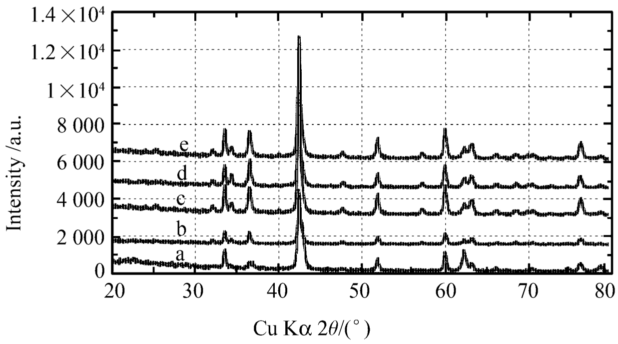

Fig. 2 XRD of these five samples. **(a)** HD-MgB_2 prepared by nanometer Mg powder, **(b)** HD-MgB_2 prepared by Mg chip, **(c)** HD-MgB_2 by Alfa Aesar Mg powder, **(d)** HD-MgB_2 prepared by ordinary off-the –shelf Mg powder, **(e)** HD-MgB_2 prepared by Alfa Aesar MgB_2 powder.

The microstructure of the five samples was observed using a Stara BD325 FIB (focus ionic beam) electronic microscope. In Fig. 3, the scanning electron micrographsare shown. The first five, from (a) to (e), are for the samples 1 to 5, while (f) is for sample 4 before the re-sintering process, denoted as sample 4a. The density of the sample 4a is as low as 1.04 g/cm^3. The corresponding micrograph shows many caves with line size of a few μm to tens of μm. By comparing Fig. 3 (d) with Fig. 3 (f), for the result after and before the re-sintering process, it is obvious that there are many large holes left before the re-sintering, while much less are remaining after the second sintering. The other four samples have similar characteristics as well. So, the re-sintering process in magnesium-rich vapor environment is a necessary procedure to obtain HD-MgB_2 sample in ambient pressure.

Table 1 The deduced crystal parameters for the 5 HD-MgB_2 superconductor samples. Also listed are parameters from some of the previous works.

Sample name	a/Å	c/Å	V/Å^3	$D_{measuring}$/(g·cm^{-3})	$D_{measuring}/D_{theory}$
Sample 1 Nanometer Mg powder	3.078(2)	3.5217(2)	86.696	2.20	0.863
Sample 2 Mg chip	3.073(2)	3.5208(2)	86.393	2.32	0.910
Sample 3 Alfa Aesar Mg powder	3.075(4)	3.515(7)	86.391	2.30	0.902
Sample 4 Ordinary off-the-shelf Mg powder	3.083	3.519	86.900	2.23	0.875
Sample 5 Alfa Aesar MgB_2 powder	3.073(6)	3.518(3)	86.353	2.28	0.894
Comparison Sample name	a/Å	c/Å	V/Å^3	Remark	
Zhu Y. [10]	3.086(5)	3.518(5)	87.085	Ambient pressure	
Cristina Buzea [9]	3.086	3.524	87.193	Ambient pressure	
B. Lorenze [2]	3.084	3.523	87.055	Prepared by High-press with high temperature	
Ren Zhi-an [5]	3.082	3.524	86.967	Prepared by High-press with high temperature	

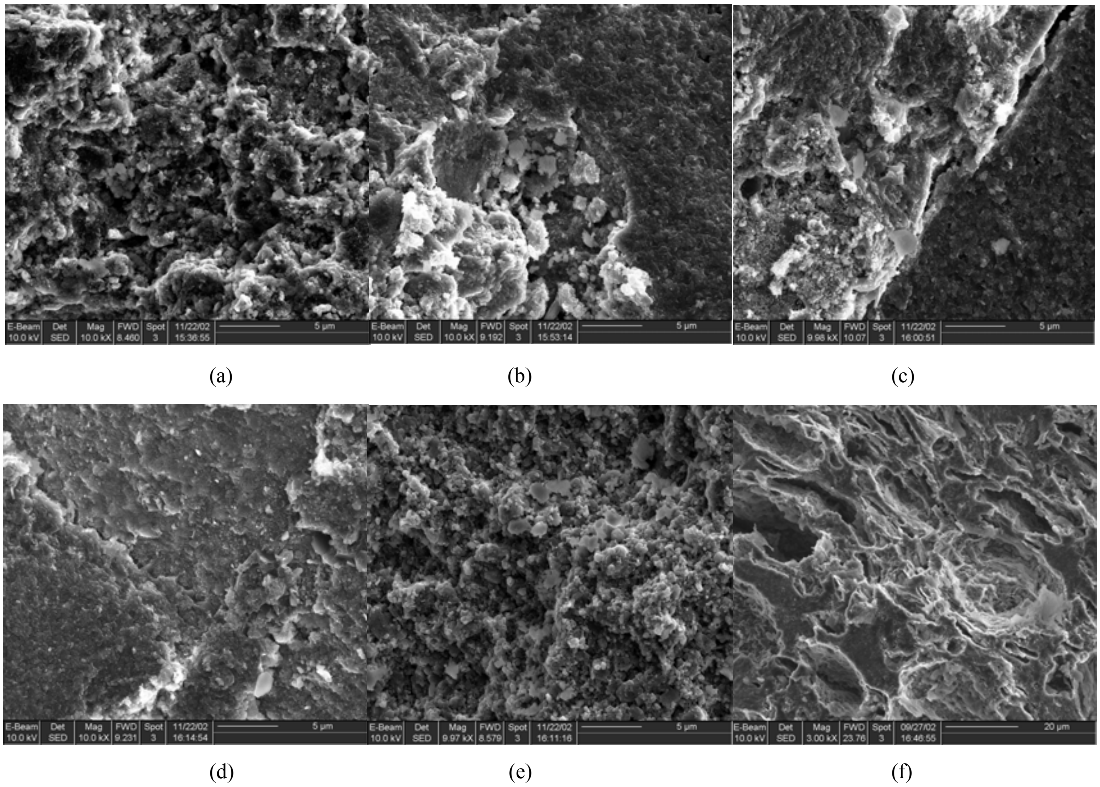

Fig. 3 The SEM photos for the five HD-MgB_2 samples magnified by about 10 000 times. **(a)** Sample 1: HD-MgB_2 prepared by nanometer Mg powder, **(b)** Sample 2: HD-MgB_2 prepared by Mg chip, **(c)** Sample 3: HD-MgB_2 by Alfa Aesar Mg powder, **(d)** Sample 4: HD-MgB_2 by ordinary off-the-shelf Mg powder, **(e)** Sample 5: HD-MgB_2 prepared by Alfa Aesar MgB_2 powder, **(f)** Sample 4a: MgB_2 sample prepared by ordinary Mg powder and boron powder finished the first sintering process, the magnification of this SEM picture is 3000 times.

Figure 4 shows the diagram of the sample block surrounded by magnesium vapor from all directions. This is rather different configuration from what is seen in Fig. 1. To achieve the scheme depicted in Fig. 4, we designed a box made from six pieces of Mg-rich MgB_2 samples. The Mg-rich box provides a homogeneous distribution Mg vapor environment in all directions during the heat treatment.

The density of the sample after the double sintering process exceeds 2.2 g/cm^3 in general. For example, the density of sample 5 after the initial sintering (750°C, 2 hours) was 1.28 g/cm^3. It increased to 2.30 g/cm^3, 90.2 % of the theoretical value, after the second sintering. In Table 1, the lattice constant of our HD-MgB_2 samples is smaller than the ones prepared by high pressure at high temperature (HP-MgB_2) and by other methods. To achieve a smaller lattice constant, the T_c of the HP-MgB_2 sample would decrease under pressure

[9]. For the HD-MgB_2 polycrystalline samples reported in the present work, the T_c remained at 39 K even with the smaller lattice constant due to the double sintering process.

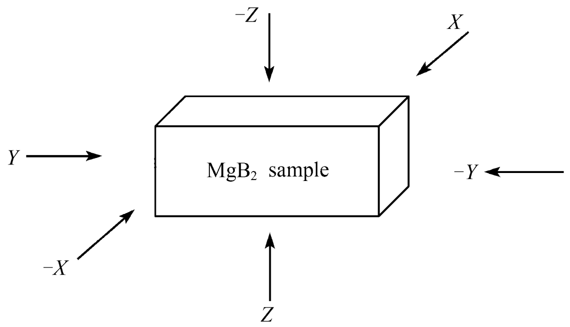

Fig. 4 Simple diagram for the diffusion of magnesium into the MgB_2 sample during the heat process.

The ZFC magnetization measurement was carried out by a SQUID magnetometer (Quantum Design MPMS). All of the five samples have T_c of 39 K with a sharp transition. This transition temperature is higher than that of the HP-MgB_2 sample reported previously [4–8]. The *M–T* curve of ZFC measurement at 20 Oe for sample 1 is shown in Fig. 5.

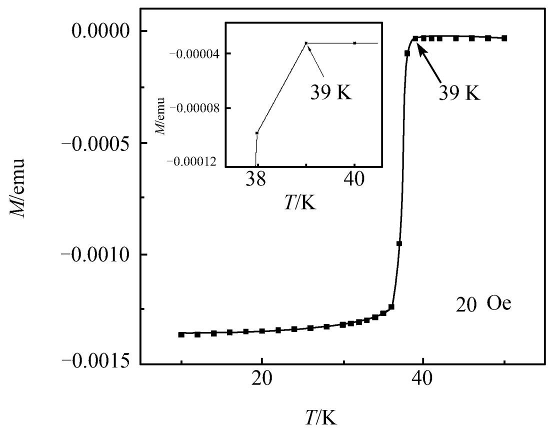

Fig. 5 Temperature dependence of ZFC magnetization measurement at the background field of 20 Oe. The T_c is 39 K with a sharp transition as shown.

4 Conclusions

The HD-MgB_2 superconductor samples prepared with magnesium raw material from different sources by the double sintering process have densities higher than 2.2 g/cm^3. Sample 2, has the highest density of 2.32 g/cm^3, which is 91 % of the theoretical value. The transition temperature is 39 K. This method provides an easy way to prepare high-density MgB_2 sample. By this method a large amount of bulk HD-MgB_2 samples can also be prepared.

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References

1. Nagamatsu J., Nakagawa N., Murannka T., Zenitani Y., and Akimitsu J., Nature (London), 2001, 410: 63
2. Lorenz B., Meng R. L., and Chu C. W., Phys. Rev. B, 2001, 64: 012507
3. Xu M., Kitazawa, Takano Y., Ye J., Nishida K., Abe H., Matsishita A., and Kido G., Preprint cond-mat/0105271
4. Deemyad S., Schilling J. S., Jorgensen J. D., and Hinks D. G., Physica C, 2001,361: 227–233
5. Ren Z. -A., Che G. -C., Zhao Z. -X., Chen H., Dong C., Ni Y. -M., Jia S. -L., and Wen H. -H., Chinese Physics Letter, 2001, 18(4): 589
6. Frederick N. A., Li S., Maple M. B., Nesterenko V. F., and Indrakanti S. S., Physica C, 2001, 363: 1
7. Jung C. U., Park M. -S., Kang W. N., Kim M. -S., Lee S. Y., and Lee S. -I., Physica C, 2001, 353: 162
8. Tanako Y., Takeya H., Fujii H., Kumakura H., Hatano T., Togano K., Kito H., and Ihara H., Appl. Phys. Lett., 78: 2914
9. Cristian Buzea and Tsutomu Yamashita, Supercond. Sci. Technol., 2001, 14: R115–R146
10. Zhu Y., Wu L., Volkov V., Li Q., Gu G., Moodenbaugh A. R., Malac M., Suenaga M., and Tranquada J., Physica C, 2001, 356: 239