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Bulk MgB_2 superconductor with high critical current density synthesized by self-propagating high-temperature synthesis method*

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Pure MgB_2 bulk samples are successfully synthesized by self-propagating high-temperature synthesis (SHS) method. The experiments show that the best preheating temperature is 250°C, the highest J_c values of the prepared MgB_2 reach 1.5×10^6A/cm^2 (10K, 0.5T) and 1.7×10^6A/cm^2 (20K, 0T), and the MgB_2 particle sizes range from 2 to 5μm. The advantages of this method are that it is simple, economical and suitable for the manufacture of bulk MgB_2 materials on industrial scale.

Keywords: SHS method, bulk MgB_2 superconductor, superconductivity
PACC: 7460M, 7460, 7460J

1. Introduction

Since the discovery of superconductivity in MgB_2 with T_c=39K,[1] this material has been prepared under a variety of conditions. The most common method is based on the solid state reaction between boron and magnesium fine powders in a sealed quartz or metallic tube of Ta or Mo. The bulk MgB_2 samples prepared under normal pressure have a low J_c of 2×10^5 A/cm^2 at 10K in a zero-field.[2,3] The high-quality MgB_2 bulk samples have been synthesized under high pressures,[4–9] their typical J_c value could reach 2×10^4A/cm^2 at 20K in a 1T field.[5] In general, the temperatures in synthesis and the times of the solid state reaction under a high pressure and normal pressure are in a range of 650–900°C and 2 to 9 hours respectively.[10] These synthesis methods require longer time and need complicated processes. Przylski *et al* synthesized MgB_2 bulks by thermal explosion method.[11] In this paper, we report a new synthesis method of bulk MgB_2, i.e. self-propagating high-temperature synthesis (SHS) technology.

2. Experiment

The magnesium and boron powders (with a purity of 99%) were mixed in a ball mill for 2 hours in a chemical ratio Mg:B=1:2. The mixture ratio of ball to the material was 35:1, and the revolving rate of the ball mill was 200r/min. The mixture was compacted into a cylindrical sample of 20mm in diameter and 60mm in height under a pressure of 100MPa. The cylindrical sample was placed in an iron crucible and heated in a furnace with a vacuum degree of 2.4×10^{-3}Pa at a heating rate of 30°C/min then rising up to 150°C, 250°C, 350°C, 450°C, 550°C and 700°. Then, the sample was ignited with an electric arc from the end to initiate the self-propagating reaction. This reaction was completed in 3–5s. Finally, the prepared sample was followed by cooling the furnace down to room temperature. In order to clearly understand the SHS method and the reaction process as well, they are shown in Figs.1 and 2 respectively.

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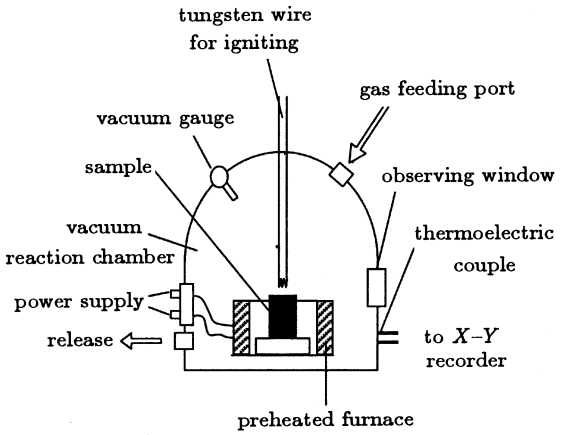


Fig.1. SHS reactor.

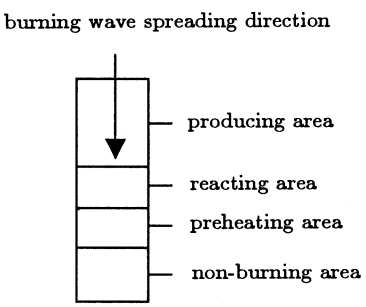


Fig.2. Schematic diagram of SHS process.

The phase analyses of the samples were carried out on the Rigaku's D/Max- 2400 type x-ray diffractometer with CuKa-radiation. The SEM observation was performed by use of the Hitachi S520 Scan Electron Microscope. The magnetizations of samples were measured using a superconducting quantum interference device (SQUID Quantum Design MPMS) at different temperatures in magnetic fields up to 7T. Magnetic J_c was deduced from hysteresis loops using the Bean Model: J_c=20delt$M/V/(a(1-a/3b))$,[12] $a, b \perp H$, $c//H$, where deltM is the difference in magnetic moment between magnetization loops at the same magnetic field in emu/cm^3, V is the volume of sample in cm^3, a (1.9), b (2.74) and c (0.5) are respectively the sizes of the measured sample in mm.

3. Results and discussion

The adiabatic temperature (T_{ad}) is the highest temperature during the SHS reaction with the heat radiation ignored. According to the empirical criterion given by Gkigorev, only when $T_{ad} > 1527°C$[13] can the SHS reaction be maintained by itself. Otherwise the energy should be complemented from outside.

The chemical reaction takes place in MgB_2 preparation as follows:

$$Mg(s) + 2B(s) \rightarrow MgB_2(s).$$

The rate of this reaction is very fast and finished only in 3–5 seconds, so, little heat diffuses out of the system. It can be regarded as a heat-insulated system. The adiabatic formula is

$$\sum m_i(H^0_{298} - H^0_{T_0})_{i(\text{reactant})} + \sum n_j(H^0_T - H^0_{298})_{j(\text{resultant})} + \Delta H^0_{298} = 0.$$

Let

$$F(T_0) = \sum m_i(H^0_{298} - H^0_{T_0})_{i(\text{reactant})} + \Delta H^0_{298},$$

and

$$F(T) = \sum n_j(H^0_T - H^0_{298})_{j(\text{resultant})},$$

select such consecutive figures (T_1, T_2) from the thermodynamic data[14] at the same temperature T_0 that $F(T_0) > F(T_1)$, and $F(T_0) < F(T_2)$, and use the way of inner insertion algorism, then we will have

$$T_{ad} = \frac{F(T_0) - F(T_1)}{F(T_2) - F(T_1)}(T_2 - T_1) + T_1.$$

Here,

$$\sum m_i(H^0_{298} - H^0_{T_0})_{i(\text{reactant})}$$

and

$$\sum n_j(H^0_T - H^0_{298})_{j(\text{resultant})}$$

are respectively the relative enthalpies of the reactant and resultant molecules, T_0 is the preheating temperature, ΔH^0_{298} is the standard enthalpy at 298K. So the adiabatic temperature T_{ad} can be evaluated at different temperatures T_0. Figure 3 shows curves of T_{ad} versus T_0. From Fig.3 it can be seen that when temperature is 25°C (room temperature), T_{ad} is 1341°C, which is lower than 1527°C. The sample must be preheated according to empirical criterion to maintain the SHS reaction. The T_0 should be above 186°C. The experimental temperature is lower than the theoretical temperature as shown in Fig.3, which is due to the fact that the system is regarded as a heat-insulated one. In fact during the reaction some heat can radiate to the outside. The difference between the two curves increases with the increase of temperature. This is because the higher the sample temperature, the more the heat radiates to the outside.

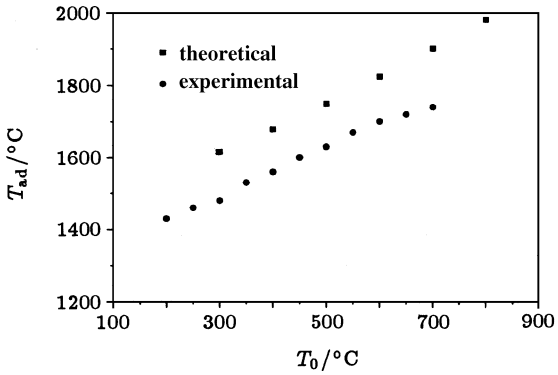


Fig.3. Adiabatic temperature (T_{ad}) versus preheating temperature (T_0).

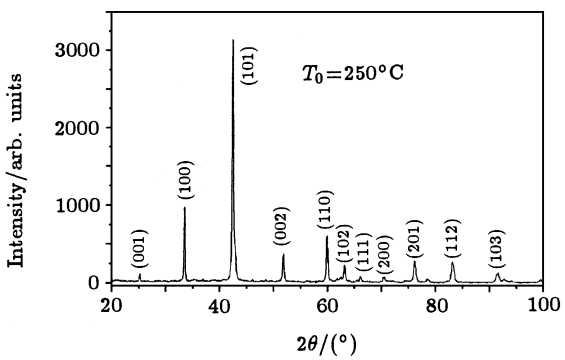


Fig.4. Typical x-ray diffraction patterns of MgB_2 bulks obtained at T_0 = 250°C.

Experimental results indicate that when preheating temperatures of the sample are 250°C, 350°C, 450°C and 550°C, single phase MgB_2 superconductors can be obtained. One of their XRD patterns is shown in Fig.4, which indicates that MgB_2 is very stable in the temperature range of 250°C–550°C. When the preheating temperature is higher than 657°C, then MgB_2 transforms into MgB_4 or MgB_7, which can be explained from the phase diagram of Mg–B system.[15]

Figure 5 shows the temperature dependence of magnetization for the MgB_2 at a magnetic field of about 2.0×10^{-3}T in the zero-field cooling (ZFC) and field-cooling (FC) modes. It can be seen that critical temperature (T_c) slightly decreases and the transition width becomes slightly larger with the preheating temperature increasing from T_c=37.4K for T_0=250°C to T_c=36.5K for T_0=550°C, which may result from the effects of a small amount of MgO and B. The best sample obtained at T_0=250°C displays a superconducting transition at 37.4K with a sharp transition width of 0.4K. Figure 6 illustrates the J_c value as a function of magnetic field at selected temperatures for the samples obtained at T_0=250°C–550°C. The samples obtained at T_0=250°C–350°C have a higher J_c than the samples obtained at T_0=550°C. The J_c value of the samples obtained at T_0=250°C is the highest among these samples. It can be seen from Fig.6 that the J_c values are 1.5×10^6 A/cm^2 in a 0.5T field at 10K, 1.7×10^6A/cm^2 in a self-field at 20K and 3.4×10^5 A/cm^2 in a 0.5T field at 30K. These J_c values are much higher than the best data of the MgB_2 bulk samples obtained by proton irradiation,[16] hot isostatic pressing[17] and high pressure synthesis. The results above indicate that the SHS is an effective and easily controlled method to improve J_c. This technique is very suitable for the manufacture of MgB_2 bulk materials industrial scale.

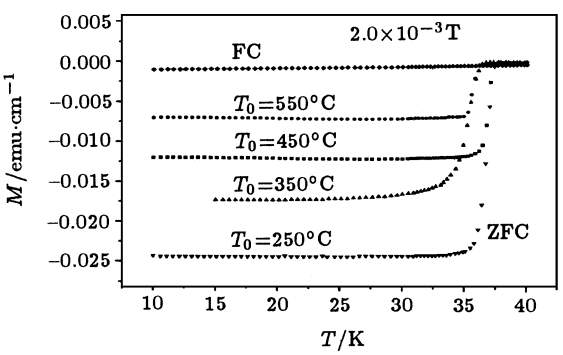


Fig.5. Temperature dependence of Magnetization in ZFC and FC for MgB_2 bulk in a 2.0×10^{-3}T field.

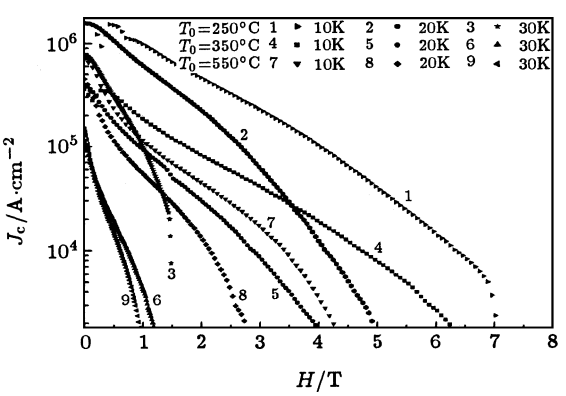


Fig.6. J_c versus magnetic field at 5K,20K,30K for MgB_2 bulk. Note that J_c is as high as about 1.5×10^6 A/cm^2 in a 0.5T field at 10K.

The SEM observation (Fig.7) indicates that the MgB_2 sample has a layered structure. There exist some cavities between layers. Each layer is formed by particulate crystalline grains with sizes of 2–5μm. The feature of this sample is almost the same as that of the sample prepared by thermal explosion.[11]

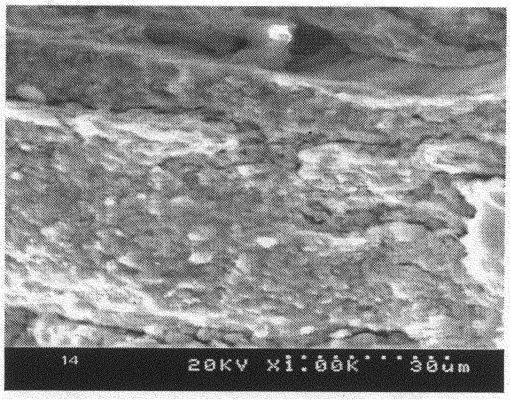


Fig.7. The SEM photography of MgB_2 bulk.

4. Conclusions

The SHS method is presented to prepare pure MgB_2 bulk materials with particulate crystalline grain sizes of 2–5μm. The experiments indicate that the preheating temperature T_0 should be above 186°C and the best T_0 is 250°C. The T_c of prepared MgB_2 is 37.4K and the transition width is 0.4K. The J_c values of the MgB_2 are significantly enhanced up to 1.5×10^6 A/cm^2 in a 0.5T field at 10K, 1.7×10^6 A/cm^2 in a self-field at 20K and 3.4×10^5 A/cm^2 in a 0.5T field at 30K. This technique is suitable for the manufacture of MgB_2 industrial scale.

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