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RAPID COMMUNICATION

Rapid preparation of MgB_2 superconductor using hybrid microwave synthesis

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Abstract

A novel hybrid microwave procedure for the synthesis of MgB_2 superconductor was demonstrated. This procedure has advantages over other methods using sealed tubes or high pressure. Using silicon carbide (SiC) powder as the susceptor, the MgB_2 samples can be synthesized in about 10 min by microwave heating. The superconducting transition width of the MgB_2 sample was less than 0.3 K, and its zero-resistance temperature was 39.5 K. The critical current density J_c estimated from the magnetization hysteresis is 4.5×10^4 A cm^{-2} at 20 K and 1 T, which is close to that of the samples prepared by high-pressure sintering.

The MgB_2 superconductor, discovered by Akimitsu *et al* [1] in 2001, has the highest T_c among simple binary compounds up to now. In addition to its high T_c, MgB_2 has other advantages for applications such as high critical current densities and the low cost of the raw materials [2–4]. However, it is not easy to prepare bulk MgB_2 samples because Mg is extremely volatile and susceptible to oxidation at elevated temperature [5]. Usually, MgB_2 bulk samples are prepared in sealed tantalum and quartz tubes or by high-pressure sintering [6]. Although these methods are very useful, they have some shortcomings for batch production due to the high costs of materials and energy.

Microwave synthesis is a very promising preparation method for many materials because it is fast, clean and energy efficient [7]. Many materials have been synthesized by the microwave method at considerably lower temperature and shorter time than the conventional methods. Using microwave heating for the MgB_2 synthesis, the evaporation and oxidation of magnesium can be significantly reduced and it is possible to avoid the limitation and expenditure of the sealed (metal or quartz) tubes. There are only two reports in the literature referring to the microwave preparation of MgB_2 [8, 9]. Unreacted magnesium is the major phase in the samples prepared by Agostino *et al* and the low reaction yield was attributed to the local inhomogeneities [8]. Sealed quartz tubes are used by Köseoğlu *et al* and their samples contain approximately MgB_2 (75%), MgO (20%) and MgB_4 (5%) [9]. In this communication, we report the preparation of MgB_2 high-quality bulk samples using a hybrid microwave processing.

The samples were prepared using stoichiometric amorphous boron (99.99% pure, 360 mesh) and magnesium powders as starting materials. Samples A and B were prepared using coarse Mg (98.5% pure, 10 mesh) and fine Mg (99.8% pure, −100 mesh) powder respectively. The starting materials of sample A are ball-milled for 2.5 h, and that of sample B is thoroughly mixed in a glass bottle by wobbling. It should be mentioned here that the average grain size of the ball-milled Mg powder in sample A is still larger than that in sample B due to the ductility of the Mg metal. The mixed powders were pressed into pellets 20 mm in diameter and 2 mm in thickness under a pressure of 15 MPa. The pellets were placed in a small alumina boat and embedded in powder of the same composition

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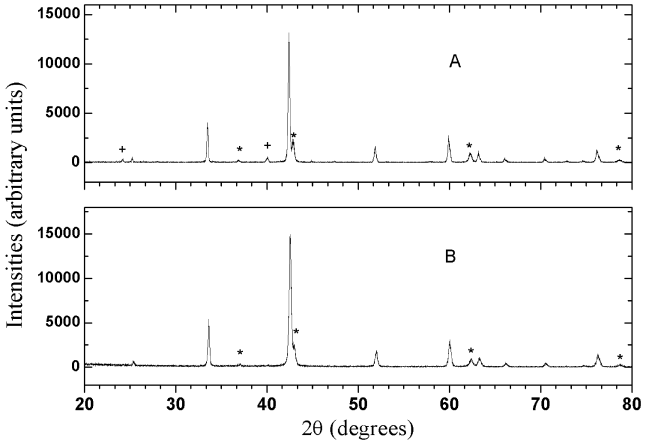

Figure 1. XRD patterns of MgB_2 samples A and B synthesized by the hybrid microwave method. The impurity peaks are labelled as * for MgO and + for unknown phases.

to protect the magnesium from oxidation. The alumina boat was placed in the middle of an alumina crucible filled with SiC powder used as the microwave susceptor. An alumina plate was used as a lid of the crucible, and an alumina tube drills through the lid to supply flowing argon (99.99% pure) to the crucible. The crucible was placed on the turntable in a modified domestic microwave oven working at the frequency of 2.45 GHz and maximum power of 800 W (Midea KE23B-W). The output power can be adjusted from 0 to 800 W at intervals of 80 W (10%). Microwave heating was carried out at the power level of 560 W (70%) in 11 min. The crucible was red hot and the maximum temperature was estimated to be approximately 800 °C. The sample was cooled down in the oven under flowing Ar gas.

The structural and composition analysis were carried out using an x-ray diffractometer (M18AHF) with Cu Kα radiation and a scanning electron microscope (XL30S-FEG). The temperature dependence of resistance was measured by a standard four-probe method with a voltage resolution of 10^{-7} V. Magnetic susceptibility was measured by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The critical current density J_c was calculated from the hysteresis data based on the Bean model using a formula for the rectangular shape samples [10]. The samples were shaped to rectangular slabs for the resistivity and J_c measurements.

Figure 1 shows the powder x-ray diffraction patterns for samples A and B. The phase analysis of the XRD patterns reveals that MgB_2 is the major phase in both samples. All impurity peaks are attributable to MgO for sample B, and other phases such as Mg and MgB_4 are below the detection limit. Additional impurity peaks (see figure 1 near 40° and other positions) in the XRD patterns indicate that sample A contains extra impurity phases. The lattice parameters of the MgB_2 are $a = 3.0837 \pm 0.0004$ Å, $c = 3.5214 \pm 0.0005$ Å for sample A and $a = 3.0841 \pm 0.0005$ Å, $c = 3.5195 \pm 0.0006$ Å for sample B respectively. Phase compositions of the samples were analysed with a Rietveld program, RIETAN 2000 [11], and the estimated mass fractions of MgO are 12.5% and 9.6% for samples A and B respectively.

The diffraction peaks of sample A are sharper than that of sample B because sample A has a larger average grain size,

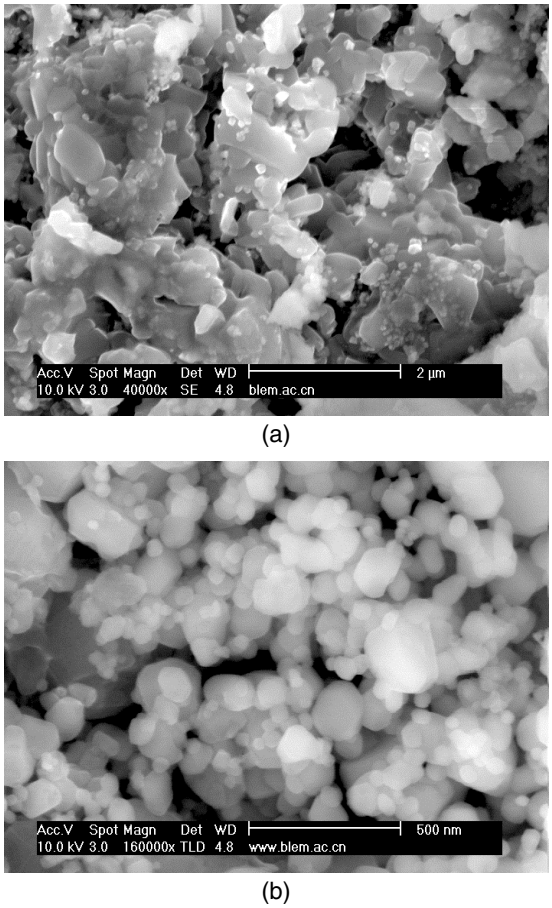

Figure 2. The SEM micrographs of the MgB_2 samples A (a) and B (b).

which is confirmed by the scanning electron micrograph. The scanning electron micrographs of the MgB_2 samples A and B are shown in figure 2. It is obvious that the MgB_2 grain sizes and shapes are greatly changed from sample A to sample B. Sample A has irregular-shaped grains with an average size of around 0.5 μm, while sample B has roughly ball-shaped grains with an average size of around 0.1 μm. The average grain size of sample A is about five times as large as that of sample B. The great change of the microstructures can be attributed to the size change in their raw materials, because other preparation conditions are unchanged. Therefore, the microstructure of the MgB_2 products can be controlled by adjustment of the grain sizes of the starting materials. It should be mentioned here that samples are porous, and the measured densities (1.08 g cm^{-3}) are approximately 40% of the calculated value (2.63 g cm^{-3}).

The temperature dependence of resistivities for samples A and B are shown in figure 3. Both samples have sharp superconducting transitions. The onset and zero-resistance temperatures of sample A are 39.8 and 39.5 K respectively, and they are about 0.1 K higher than that of sample B. The residual resistivity ratios (RRRs) are 4.41 and 3.63 for samples A and B respectively. The higher resistivity and lower RRR of sample B signify its higher lattice defects. Major defects in sample B are grain boundaries due to its tiny grain sizes.

Figure 4 shows J_c as a function of applied magnetic field for samples A and B at 20 and 30 K. The J_c of sample B is obviously higher than that of sample A, and this can be explained by the grain size effect. Smaller grain size in

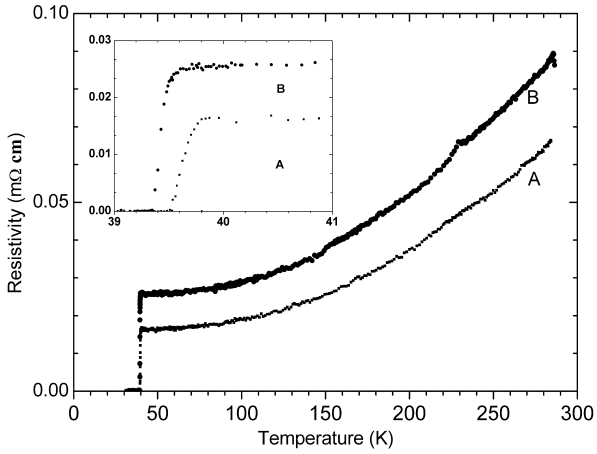

Figure 3. The temperature dependence of resistivities for the MgB_2 samples A and B.

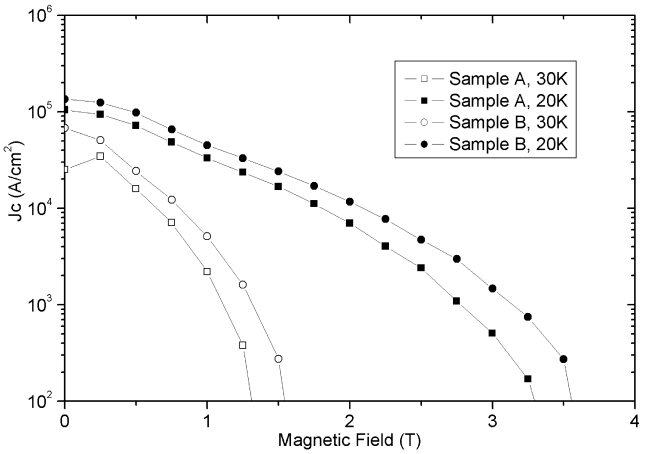

Figure 4. The critical current densities at 20 and 30 K as a function of applied magnetic field for MgB_2 samples A and B.

sample B generates more grain boundaries as effective pinning centres [4]. Consequently, sample B shows enhanced J_c. At $T = 20$ K and 1 T, the J_c of sample B (4.5×10^4 A cm^{-2}) is approximately 90% of the J_c value of the samples prepared by high-pressure sintering. Taking the porosity into account, it is possible to increase J_c of the samples by subsequent hot isostatic pressing.

Finally, we would like to highlight the temperature measurement problem and point out some possible ways to solve it. Because the reactor was placed on the turntable in the microwave oven and it was rotating during the microwave heating process, it is difficult to monitor the temperature directly using a thermocouple. The temperature was measured by interrupting the microwave irradiation and inserting a thermocouple into the SiC powders. The maximum temperature thus obtained was only 700 °C, and this is estimated to be about 100 °C lower than the actual temperature. The trial and error method was used to determine the proper synthesis conditions in our experiments. According to our experiences, when the reaction temperature is relatively low, un-reacted Mg exists in the samples; when the reaction temperature is relatively high, the MgB_4 phase appears. Therefore, it is not complicated to find the proper heating conditions. When the sample was heated to its 'ignition' temperature, the reaction can rapidly proceed, similar to a self-propagation combustion because the formation of MgB_2 from Mg and B powders is exothermic. However, temperature measurement during the microwave heating is important to understand the real conditions for the MgB_2 formation. In order to solve the problem of the temperature measurement, we will use a microwave oven with a rotating antenna instead of a turntable in our future experiments.

In summary, we have synthesized MgB_2 bulk materials using a hybrid microwave method. The obtained MgB_2 samples are superconducting with the onset temperature above 39 K. Samples made by the hybrid microwave method show high J_c comparable to that of samples prepared by high-pressure sintering. Using this method, the evaporation and oxidation of magnesium are significantly reduced and the limitation and expenditure of the sealed tubes are avoided. The microwave synthesis method of MgB_2 described here has the potential to produce fine powder for fabrications of MgB_2 tapes and wires, and it can also be easily applied to make various doped MgB_2 samples to study the doping effects.

Acknowledgments

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