Korean J. Chem. Eng., **20**(6), 1183-1187 (2003)

Preparation and Characterization of Magnesium Diboride Superconductor by Melting Process

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(*Received 16 October 2003 • accepted 7 November 2003*)

Abstract–The recent discovery of the binary metallic magnesium diboride (MgB_2) superconductor having a remarkably high transition temperature (T_c) of 39 K has generated excitement among the scientist worldwide and gained great scientific interest. Various methods (viz. PLD, solid state reaction etc.) are reported for the preparation of this material in different forms (bulk, wire, thin film) which require a high processing temperature (750 to 950 °C). In this paper, we report a new method of processing MgB_2 superconductor that meets all the properties when compared with other processes. In this work, polycrystalline MgB_2 was prepared by using melting process at low temperature (660 °C). The stoichiometric mixture of Mg-rich and B-rich was pressed into pellets and piled to form Mg-rich/B-rich/Mg-rich system. The piled specimen was then heated up to 800 °C for four hrs with a heating rate of 5 °C/min. The sample was then kept at 660 °C for 12 hrs after cooling from 800 to 660 °C in 30 min. For comparison, the sample was also sintered at 660 °C for 24 hrs. The samples were characterized by using XRD, EDX, SEM, four probe AC methods and magnetization measurements using SQUID magnetometer. The critical temperature was found to be 39 K which shifts towards lower temperature with increasing applied field (0 to 9T). The critical current density, according to Bean's critical state model was estimated and found to be ~10^5 A/cm^2, which is comparable to the reported data.

Key words: MgB_2, Superconductor, Melting Process, Critical Temperature, Piled Specimen

INTRODUCTION

The un-expected discovery of superconducting properties of MgB_2 at high transition temperature (~39 K) [Nagamatsu et al., 2001] has produced an explosion of interest resulting in tremendous research efforts concentrating on optimizing and understanding physical properties and synthesis. The origin of high T_c in this material seems to be associated with the light boron atoms whose phonon frequency spectrum plays an important role in enhancing the electron-phonon interaction. The simple crystal structure (as compared to the copper oxide based high temperature superconductors) [Kim et al., 1995, 2003; Sun et al., 1997], the low cost of the starting material, the metallic charge carrier density and the strong coupling of the intergrains in the polycrystalline form of MgB_2 make this material a very promising candidate for technological uses, although the low value of irreversibility field and the steep decrease and the critical current density (J_c) with increasing magnetic field considerably lessen its potential for applications. However, the growth of the film is complicated by the large differences in vapor pressure (and possibly mobility and adsorption coefficient) between boron and magnesium [Jung et al., 2001a; Nagamatsu et al., 2001].

Various methods are reported for the preparation of this binary material in different forms (bulk, wire, tapes, thin film) using various technologies, viz. pulsed laser deposition, arc melting, conventional solid state reactions etc. Canfield et al. have shown a method to convert commercially available boron fibers into very low resistivity wires and Takano et al. have measured the current carrying capacity of the hot-pressed pellets. Joshi et al. have studied the superconducting properties of MgB_2, prepared by heating process, in the temperature range of 2-50 K.

The high volatility of magnesium and low decomposition temperature of MgB_2 create difficulties for the preparation of smooth, homogeneous and epitaxial thin film. To overcome this problem and to reach the bulk value of the transition temperature, ex-situ methods have been exploited. To date, reports on superconducting MgB_2 films with the highest zero resistance transition temperatures T_{c0} of up to 39 K, are based on magnesium diffusion into a boron or Mg-B film at temperatures of 900-950 °C and at high pressures [Canfield et al., 2001; Jung et al., 2001a, b; Takano et al., 2001].

According to the temperature-composition phase diagram of Mg-B system the crystal growth of MgB_2 is possible from the Mg-rich compositions at the temperature range where MgB_2 co-exists with the gas and liquid phases. Indeed, in 1973 the vapor transport method was utilized for crystal growth of MgB_2 and MgB_4 phases. The MgB_2 crystals were obtained by isothermal heat treatment of Mg-rich composition at 1,200-1,400 °C and Mg vapor pressure 1-8 bar in a sealed Mo container. It is worth noticing that all the reported methods/techniques require high processing temperature (above 750 to 950 °C).

In the present work polycrystalline MgB_2 was prepared by using the melting process at a comparatively low temperature (660 °C), than reported, in the pellet form of Mg-rich/B-rich/Mg-rich structure. The samples were characterized by using XRD, EDX, SEM, and four probe AC methods. The magnetization studies were carried out by using a SQUID magnetometer in the temperature range

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of 10-30 K and in the magnetic field up to 6 Tesla. The results are compared and discussed with the reported data.

EXPERIMENTATION

The MgB_2 sample was prepared by mixing the stoichiometric powders of Mg and B (99.999% and 99% pure, STREM chemicals). The powders were pressed into three tablets in a mixing ratio of Mg : B as 2 : 1, 1 : 4 and 2 : 1 at the pressure of ~200 Mpa. Various ratios of Mg : B combination were tried in order to achieve the expected superconducting properties. It was realized that this particular combination gives the best superconducting properties, comparable to reported work [Joshi et al., 2001; Jung et al., 2001a; Takano et al., 2001]. Each tablet was 1 mm thick and of 10 mm diameter. The three individually pressed tablets were then piled in Mg-rich/B-rich/Mg-rich structure [Park et al., 1998]. This piled specimen was then heated to 800 °C, which is the optimized temperature for this composition, with a heating rate of 5 °C/min and kept for four hrs at this temperature. The specimen was then kept at 660 °C for 12 hrs after cooling from 800 to 660 °C with a cooling rate of 5 °C/min. Hereafter, this process is referred to as the melting process. For comparison, the piled specimen was sintered at 660 °C for 24 hrs (further referred to as the sintering process).

Differential thermal analysis of the specimen was performed to find the decomposition temperature, and the corresponding curve is shown in Fig. 1. It is observed that it starts decomposing above 510 °C. Based on this, 660 °C was chosen as the calcination temperature.

Bulk X-ray diffraction was carried out by using CuK radiation in the Bragg angle ranging from 20 to 80 degrees. Information about the surface morphology and particle size was obtained by using a scanning electron microscope (Hitachi 650). The compositional details of the sample were obtained by using EDX.

The resistivity as a function of the temperature was measured by the AC four-probe method. Magnetization on the sample was measured by using SQUID magnetometer (Quantum Design) in the temperature range of 10-30 K and in the applied fields up to 6 Tesla.

RESULTS AND DISCUSSION

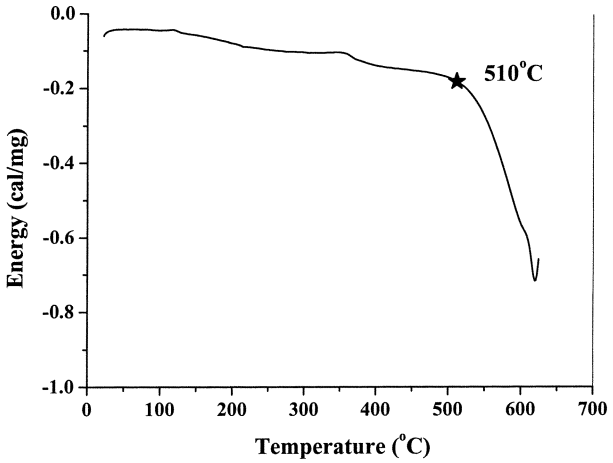

Fig. 1. Differential thermal analysis of the piled specimen.

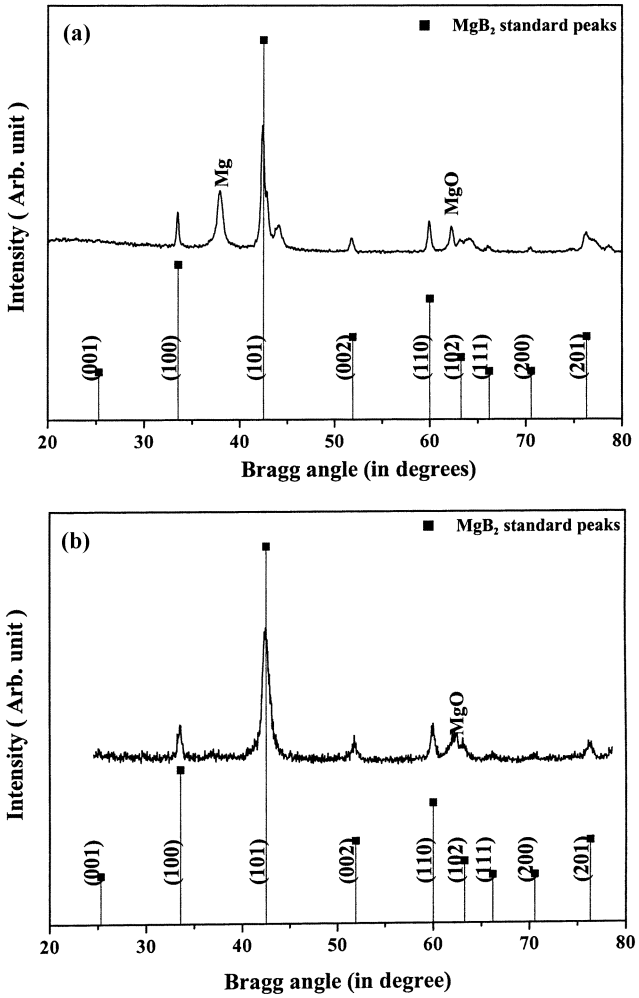

Fig. 2. Bulk X-ray diffraction pattern of sample prepared by (a) melting process and (b) sintering process.

Fig. 2(a and b) presents the X-ray diffraction patterns of the specimen prepared by the melting as well as the sintering process. It is clearly seen that the sample largely consists of the desired MgB_2 phase in both the cases. A peak of MgO is also seen which might be due to the Mg-rich pellets on either side of the piled specimen. EDX analysis shows ~70% of B and ~30% of Mg. The elemental mapping was also carried out (using area analysis) in order to understand the spread or homogeneity of the Mg and B atoms, using EDX. This analysis was carried out at the center of the pellet after making a cross section. The mapping was carried out over an area of ~60×60 micro-m^2. Fig. 3(a) shows the cross section SEM image of the pellet taken at the center. The image was taken at very low magnification in order to study big area for qualitative as well as quantitative analysis using EDX. Fig. 3(a and b) shows the scatter of the Mg and B atom, respectively. It can be seen that the atoms are spread and mixed uniformly. From quantitative analysis it is found that the sample consists of ~70% of B and ~30% of Mg. Similar analysis was carried out at many points from top to bottom of the pellet and it was found that the composition remains almost the same (with a variation of ~1% of elemental composition). This indicates that the elements are mixed well. The presence of MgO hampers the superconducting properties of the formulated material provided

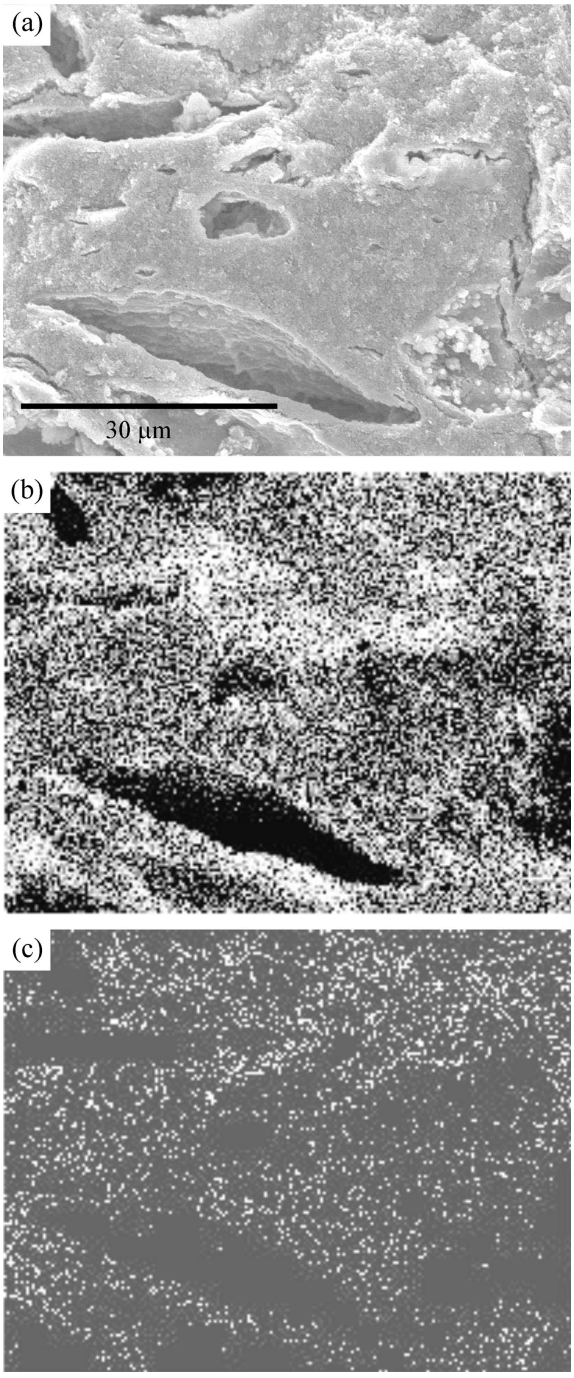

Fig. 3. Cross section SEM image of the sample prepared by melting process. Distribution of (b) Mg atom and (c) B atom, at the center of the pellet over ~60×60 μm^2 area.

the percentage is high. In the present work, only a small peak of MgO is seen indicating that the portion is small (we did not estimate the exact portion).

Fig. 4(a and b) shows the scanning electron micrographs of the specimen prepared by the melting and sintering processes. Particles of uniform shape and size are seen in the case of the sample prepared by melting whereas voids and particle agglomeration are seen in the case of sintered samples. The melting process gives a particle size of ~150 nm with a uniform distribution of particles.

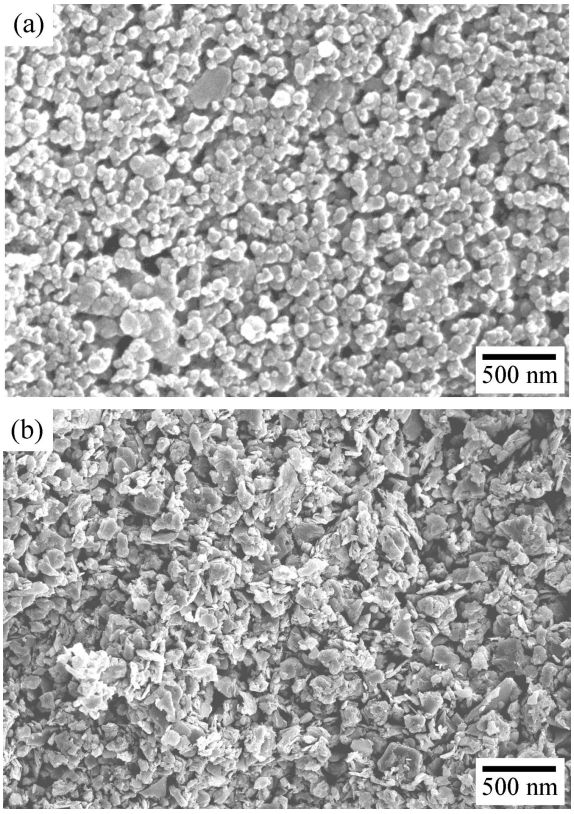

Fig. 4. Scanning electron micrographs of the specimen prepared by (a) melting and (b) sintering process.

Fig. 5(a) shows the variation in the resistivity of the sample, prepared by melting process, as a function of operating temperature (in Kelvin) at 0 Tesla. The transition temperature of the specimen is found to be 39 K, and the transition width is about 1 K for a 10-90% drop of the resistivity curve. The inset in Fig. 5(a) shows a variation at lower temperature range. The overall temperature dependence of the resistivity follows a second order function of temperature. Similar resistivity behavior has also been observed by other researchers [Jung et al., 2001a]. When samples are studied under various magnetic fields (0 T to 9 T), it is found that the transition temperature shifts to the lower side (from 39 K to 16 K) and the corresponding data are presented in Fig. 5(b) as a function of the variation in resistance with temperature. The transition width increases from 1 K to ~7 K with increasing field.

Magnetization on the sample was measured by using a SQUID magnetometer (Quantum Design) with temperature ranging from 10 to 30 K and the applied field was increased to 6 Tesla. Fig. 6(a and b) shows the magnetization hysteresis loops (M-H curves) obtained at 10 K, 20 K and 30 K of the samples prepared by melting and sintering process, respectively. It is observed that the variation in magnetization with applied field follows the trend as reported by many researchers above 20 K. The trend at 10 K is different especially at low applied fields. The reason for such behavior may be due to unlocking of the SQUID loop as the maximum range for SQUID is ±5 emu. It can be seen that magnetization value at 10 K crosses ±5 emu.

The super current density according to Bean's critical state model is given by $\mathbf{J_c=30\Delta M/d}$, where ΔM is the hysteresis of the mag-

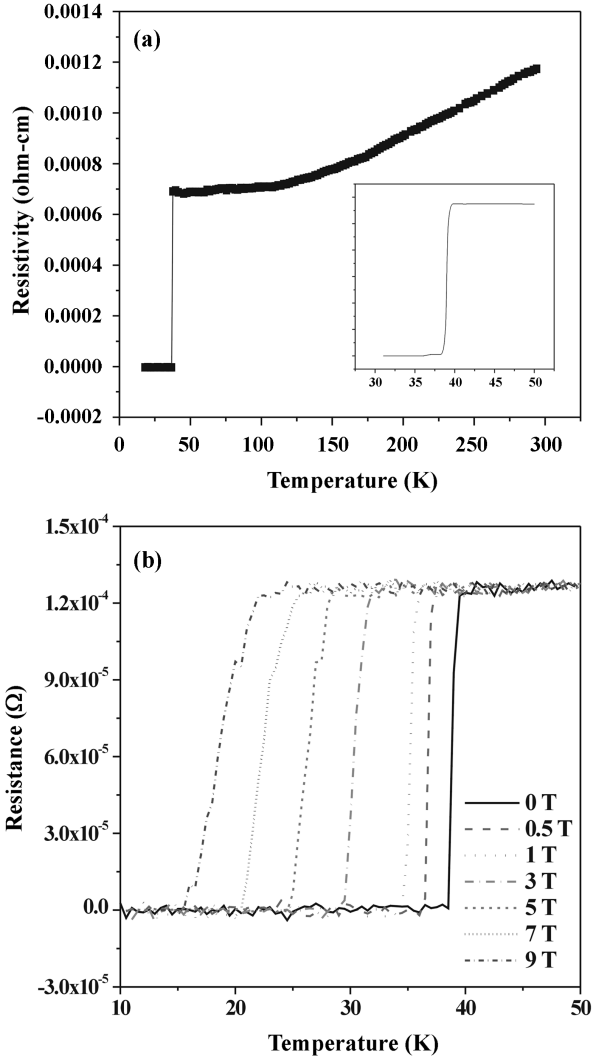

Fig. 5. (a) Variation in the resistivity of the sample, prepared by melting process, as a function of operating temperature (in Kelvin) at 0 Tesla field. Inset shows the variation at lower temperature. (b) Variation in the resistance of the sample, prepared by melting process, as a function of operating temperature (in Kelvin) at varying field (0 to 9 T).

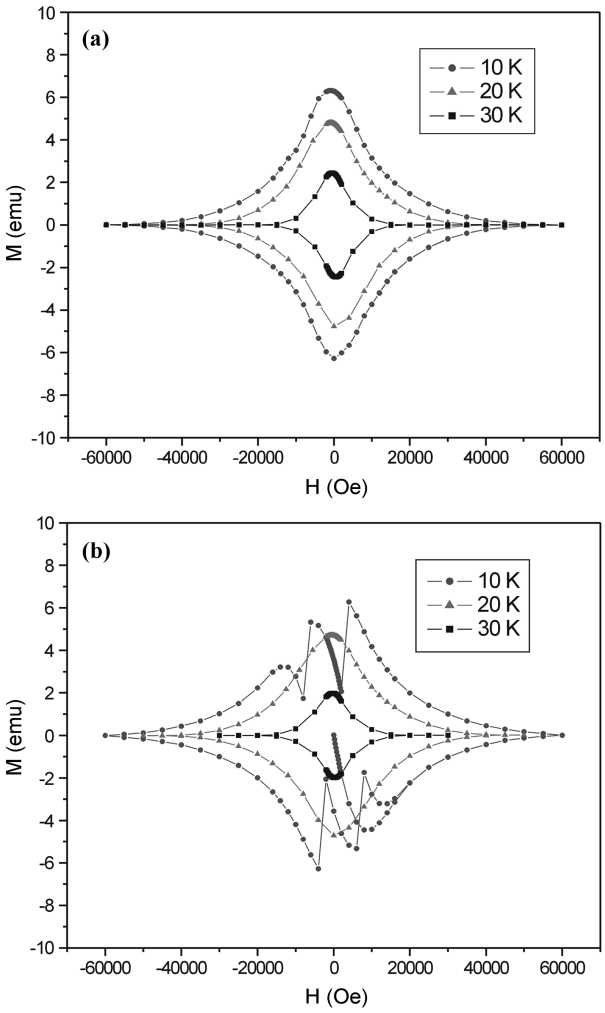

Fig. 6. The magnetization hysteresis loops (M-H curves) obtained at 10 K, 20 K and 30 K for the sample prepared by (a) melting process and (b) sintering process.

netization per unit volume (emu/cm^3) at a given field and d is the mean size of the particles. Assuming an average particle size (~15× 10^{-3} cm) and grains being insulated from their neighbor, the critical density obtained at various fields and temperatures is plotted in Fig. 7. It is seen that the critical densities are fairly large and are of the same order of magnitude as reported elsewhere [Amish et al., 2001; Wen et al., 2001]. In case of MgB_2, it is well known that the intergrain coupling is good; therefore, there can be a difference in the J_c value depending on the assumption of particle sizes.

CONCLUSION

In the present work polycrystalline MgB_2 was prepared by using the melting process at low temperature (650 °C) by preparing the piled specimen of Mg-rich and B-rich pressed pellets to have Mg-rich/B-rich/Mg-rich structure. From diffraction analysis it was

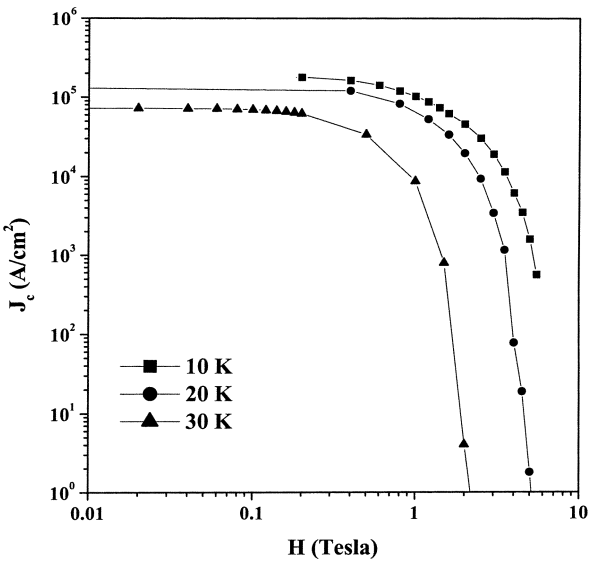

Fig. 7. The critical density obtained at various fields and temperatures using Bean's critical sate model for the sample prepared by melting process.

found that sample largely consists of the desired MgB_2 phase. SEM image shows a uniform shape and size distribution of particles prepared by the investigated method. The transition temperature of the specimen was found to be 38 K and the transition width was about 1 K for a 10-90% drop of the resistivity curve. The transition temperature shifts to the lower side when tested at increasing field. M-H studies show that the sample follows the variation trend as reported elsewhere. According to Bean's critical state model, the critical current density is fairly large (~10^7 A/cm^2) and is comparable to the reported data. In conclusion, it can be said that the MgB_2 can be processed by the suggested method, meeting all the properties when prepared by conventional methods with the advantage of low temperature processing.

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