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SYNTHESIS OF MgB_2 FROM MgB_4 THROUGH COMBINATORIAL SOLID STATE REACTION ROUTES

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ABSTRACT

MgB_4 was first prepared from the elemental magnesium and boron powders, followed by acid-washed in order to remove the primary impurity of MgO. In the second step, appropriate amount of Mg was added into the MgB_4 powders and sintered in the temperature range of 650°C to 950°C for 8 hours. XRD spectra showed that MgB_2 appeared as the main phase. The relative intensity fraction for MgB_2 was found to decrease while this value was increased for MgB_4 and MgO upon increasing the sintering temperature. Scanning electron microscopy showed a denser microstructure compared to samples prepared by direct *in-situ* reaction of (Mg + 2B). The density was found to decrease with increasing sintering temperature possibly due to the loss of Mg.

Keywords: MgB_2; superconductor;

INTRODUCTION

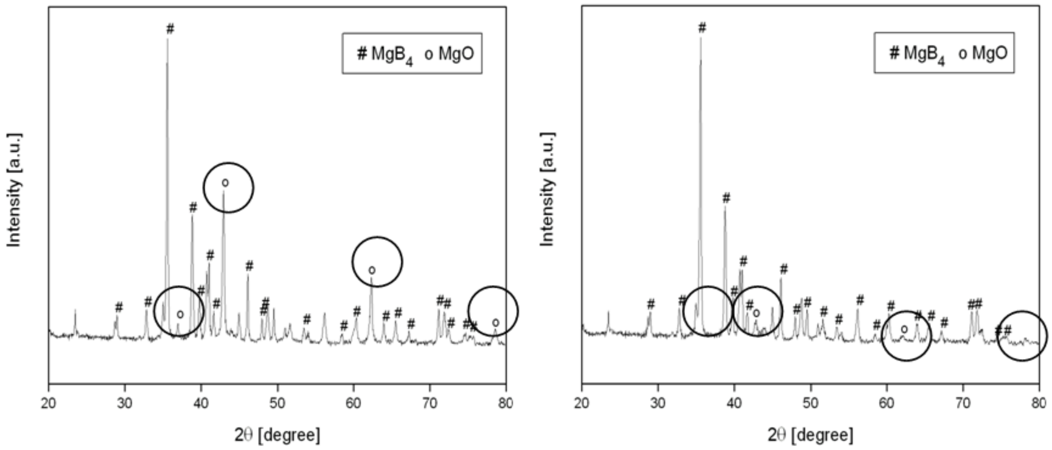
Magnesium diboride (MgB_2) was discovered to be superconducting at 39K [1]. Due to its simple crystal structure, high critical transition temperature, T_c and critical current density, J_c, it has become a potential material for various applications. The relatively cheaper cost of magnesium and boron powders compared to niobium (low-T_c superconductors) and ease of sample preparation are also the additional merits for MgB_2 from the industrial point of views. Recently, synthesis of MgB_2 by reaction of MgB_4 and Mg has been reported to yield higher purity as compared to direct *in situ* reaction of Mg + 2B [2]. Tan et al. found that the density of pure MgB_2 obtained from by this reaction method is about 1.6 g/cm^3 while the relative quantities of MgB_4 and MgO are 10.4% and 13.1%, respectively [3]. The most common impurity, MgO (can be discovered in nearly all preparations) has been decreased to a minimum. Therefore this new reaction channel may improve the method of synthesis for pure MgB_2. The aim of this work is to carry out systematic study on synthesizing highly pure and denser MgB_2 samples by reaction of MgB_4 + Mg in a varying sintering temperature and time. The effects of heat treatment on the phase formation of MgB_4 and MgB_2 are presented.

EXPERIMENTAL PROCEDURE

MgB_4 were prepared by direct *in-situ* reaction between Mg (99.7%, 14-20μm) and B (95-97%, less than 1μm) in the nominal stoichiometry of Mg:B = 1:4. Both powders are from Tangshan Wei Hao, China. They were mixed and ground, followed by pelletization. A high temperature was required to synthesize MgB_4 and an attempt had been done in the temperature range of 950°C to 1200°C. Due to the high sintering temperature, a large amount of MgO was formed in those samples. In order to remove the MgO, acid washed was performed and a "cleaner" sample of MgB_4 was obtained. Later, appropriate amount of Mg was added into the MgB_4 powders to reach a nominal stoichiometry of Mg:B = 1:2. The mixture was ground and pelletized before loading into a furnace for sintering at 650°C to 950°C for 8 hours. The samples were inspected by powder x-ray diffraction (XRD) using an X'Pert Pro Pan Alytical PW 3050 Diifractometer. The density of the samples was measured by first obtaining the mass and then dividng it with respect to the volume. Microstructure observation was done by using LEO 1455 VP SEM.

RESULTS AND DISCUSSION

Figure 1 (a) shows the XRD pattern of the optimized MgB_4 samples which were sintered at 1050°C for 2 hours. MgB_4 appears as a primary phase with MgO as the secondary phase. The high sintering temperature in prolonged time produced a relatively larger amount of MgO and this was inevitable due to the presence of residual O_2 during the sintering [2]. Moreover, the starting Mg or B powder may have already been oxidized during storage. The MgO impurity was then removed by immersing the samples in HNO_3 solution for 5 minutes. As shown in Figure 1 (b), the (200) and (220) peaks of MgO were reduced to a much lower intensity whereas the (111) and (222) peaks were totally eliminated. Thus, a "cleaner" sample of MgB_4 was obtained and can be used later for synthesizing MgB_2. Figure 2 shows the XRD patterns of (MgB_4 + Mg) powders reacted in the temperature range of 650°C - 950°C for 8 hours. MgB_2 appeared as the main phase with some MgB_4 and MgO peaks except for sample sintered at 950°C. Upon increasing the heat treatment, the intensity of MgB_4 peaks was increased while a reduction in MgB_2 peak intensity was observed.



a) Before acid-wash

b) After acid-wash

Figure 1: XRD patterns of MgB_4 sintered at 1050°C for 2 hours; before and after acid-wash by using HNO_3 in the immersing time of 5 minutes

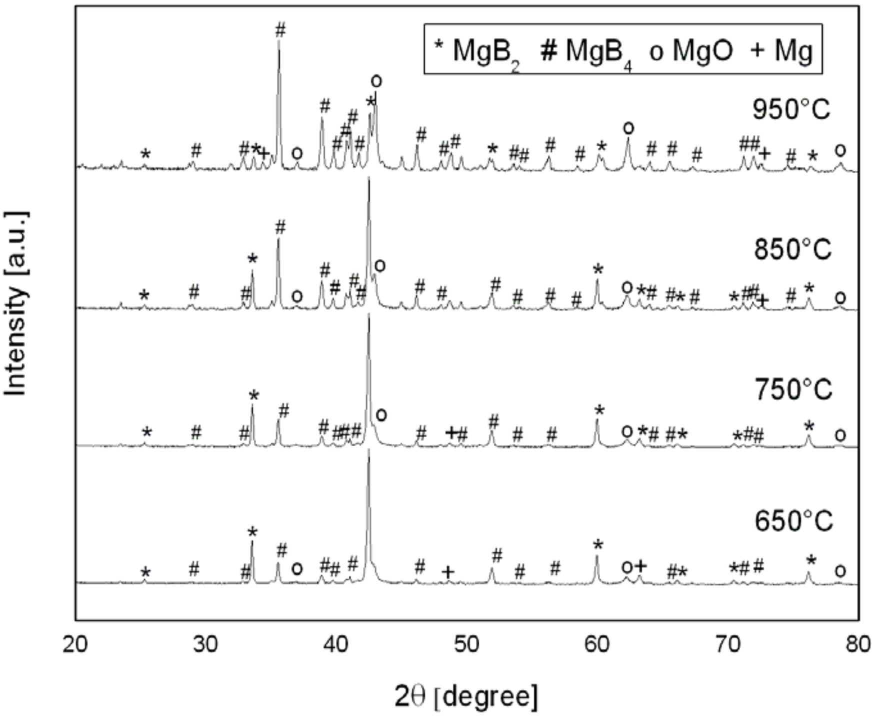


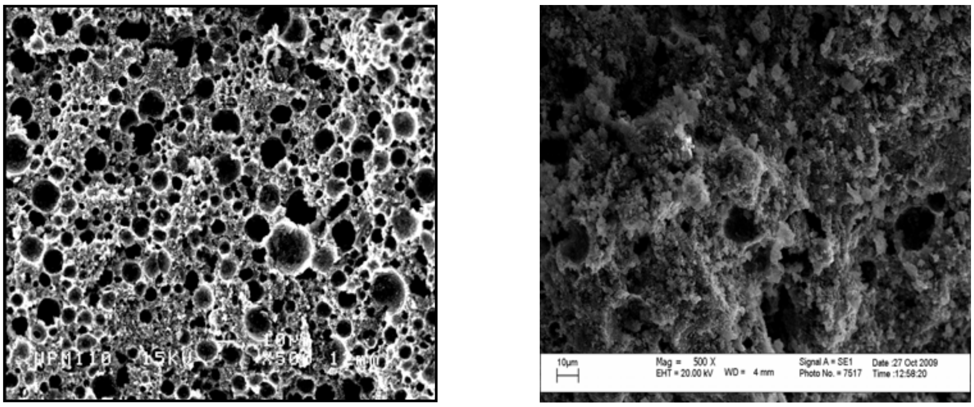
Figure 2: XRD patterns of the samples (MgB_4 + Mg) sintered at 650°C to 950°C for 8 hours

The x-ray intensity fraction of MgO and MgB_4 was calculated according to reference [4] and the related values are presented in Table 1. The lowest relative intensity of MgO and MgB_4 falls on samples sintered at 650°C at 8 hours indicating the highest volume fraction of MgB_2 phase. It can be noticed that the relative intensity of MgO phase is increased upon increasing the sintering temperature and was caused by the more severe oxidation because of the residual oxygen.

Table 1: The relative intensity fraction of MgO and MgB_4 and the density at various sintering temperature

Temperature	MgO (%)	MgB_4 (%)	Density (g/cm^3)
650°C	4.28	13.77	1.39
750°C	4.92	17.09	1.37
850°C	9.54	35.12	1.27
950°C	36.91	69.25	1.27

Table 1 also shows the variation of the density as a function of sintering temperature. Upon increasing the temperature, the density was decreased from 1.39 g/cm^3 to 1.27 g/cm^3. The evaporation of more magnesium at higher temperature resulted in a great loss of mass that could have indirectly influenced the formation of pores leading to the lower density of samples sintered at high temperature. The theoretical density of MgB_2 is 2.60 g/cm^3, which is doubled the density obtained from this work and it is expected that these samples contained a lot of pores.



a) (Mg + 2B) b) (MgB_4 + Mg)

Figure 3: The microstructures of samples prepared from a) (Mg + 2B) sintered at 650°C for 1 hour b) (MgB_4 + Mg) sintered at 650°C for 8 hours

The morphology of the samples prepared by direct *in-situ* (Mg + 2B) and (MgB_4 + Mg) were also investigated. The larger fraction of porosity is noticeable in the samples sintered from (Mg + 2B) but much less porosity was found in (MgB_4 + Mg) samples. This shows that the (MgB_4 + Mg) samples appeared to be denser compared to those prepared from direction reaction of (Mg + 2B). The pores are observed to be spherical typically and their size and shape are comparable to those of the magnesium powder used in this study. The diffusion process of Mg is relatively faster than B due to the lower melting point of Mg as compared to B and therefore the Mg sites is more favorable for pore formation [5].

CONCLUSIONS

The synthesis of pure and denser MgB_2 from (MgB_4 + Mg) was explored. The optimization of phase formation was done at 1050°C for 2 hours as shown by the XRD pattern that relative peak intensity of MgB_4 is the highest in this sintering condition while MgO appeared as the main impurity. MgO was removed later by immersing the powders into HNO_3 solution for 5 minutes. MgB_2 phase reached its highest purity level at 650°C sintered for 8 hours. The density was found to decrease as the sintering temperature increased due to the loss of Mg. Finally, the MgB_2 samples synthesized from (MgB_4 + Mg) have less porosity and look denser compared to those obtained by direct in situ reaction of Mg + 2B.

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