JOURNAL OF MATERIALS SCIENCE **39** (2004) 4893–4898

Effect of synthesis temperature on density and microstructure of MgB_2 superconductor at ambient pressure

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The experimental thermodynamic of MgB_2 synthesis process and phase compositions have been investigated by diffraction thermal analysis (DTA) technology and X-ray diffraction. The fabrication of MgB_2 bulks and superconducting properties at the temperatures range from 600 to 800°C were reported. And microstructure of MgB_2 bulks were observed by scanning electron microscope (SEM). A method was developed to determine the porosity of MgB_2 and the highest density can be obtained in MgB_2 prepared at 650°C at ambient pressure. It is found that the vapor pressure of Mg increases remarkably at high temperature, leading to the high porosity in MgB_2 samples. MgB_2 bulk with good superconducting property and fine microstructure was synthesized at 750°C.

1. Introduction

The discovery of superconductivity at 39 K in MgB_2 has attracted a lot of interest in the world since critical temperature of MgB_2 is the highest in the intermetallic superconductors [1–5]. Also, the chemical composition and crystal structure are very simple as compared to high temperature superconductors (HTS). Recently, many results on the structure, magnetic and transport properties of bulks and wires have been reported [2–9]. Unlike HTS, the high critical current densities (Jc) in polycrystalline MgB_2 materials indicate that Jc is not limited by grain boundaries, suggesting that MgB_2 has a good potential for electrical engineering applications [10]. However, Jc of MgB_2 prepared at ambient pressure is relatively low compared to A15 superconductors. The reason is attributed to the low density and the lack of flux pinning centers. It is reported that high density MgB_2 bulk samples can be obtained by high pressure synthesis [11–15], but this process is not available to prepare MgB_2 wires and tapes. Unfortunately, because of the high volatility of Mg at elevated temperature, it is very difficult to fabricate MgB_2 with high density at ambient pressure. The MgB_2 wires prepared by powder in tube (PIT) method at ambient pressure have 25% lower density than dense bulk samples fabricated under high pressure [16]. Therefore, it is still a big challenge to synthesis MgB_2 superconductor with high density at ambient pressure in order to remarkably improve superconducting properties. One of the key problems is to obtain the clearly thermodynamic characteristics of Mg-B system. Although the thermodynamics of Mg-B system were calculated by the phase diagrams modeling technique [17], no detail of experimental thermodynamic information is available in the literature until now. However, it is very necessary and important to understand the thermodynamic behavior of Mg-B system for preparation of high quality MgB_2 bulks, thin films, wires and tapes. In this paper, a series of MgB_2 bulk samples were fabricated under different conditions at ambient pressure. The diffraction thermal analysis (DTA), X-ray diffraction pattern (XRD) and scanning electron microscope (SEM) were employed to characterize these samples. Also, we developed a method to determine the porosity of MgB_2 and optimized the process to obtain high density MgB_2 samples.

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2. Experimental details

All the MgB_2 bulks samples were fabricated by standard solid state reaction technique at ambient pressure. A stoichiometric mixture of Mg powder (with purity 99%) and submicron amorphous B powder (with purity 99%) was well ground in an agate mortar for 1 h and then pressed into cylindrical pellets with a diameter of 12 mm. Five pellets settled in Al_2O_3 crucibles were placed in quartz tube respectively. To prevent oxygenation Mg powder and B powder, the quartz tube was vacuumized until 3×10^{-3} Pa and then filled with pure argon. The samples were sintered at 600°C, 650°C, 700°C, 750°C, 800°C under pure argon atmosphere for 2 h. Then all the samples were quenched to room temperature under pure argon atmosphere in 20 min.

In order to get the thermodynamic information of MgB_2 synthesis process, the diffraction thermal analysis (DTA) experiment was taken for mixture powder with the stoichiometric Mg:B = 1:2. Powder X-ray diffraction (XRD) with Cu K_α radiation was employed to characterize the samples. The critical transition temperature (T_c) of MgB_2 bulks were determined by resistance-temperature method. A volumetric method was developed to measure the porosity of MgB_2 bulks. The MgB_2 bulks were sealed in Cu cube and vacuumized until the vacuum degree to 2×10^{-3} Pa. Then the pure alcohol was filled into the Cu cube and kept for 1 h to ensure the sufficient infiltration of alcohol into MgB_2 bulks. The volume of alcohol, which equals to the volume of voids in MgB_2 bulks, can be determined by the weight change of MgB_2 bulks. The porosity was calculated by the ratio of the volume of alcohol absorbed by MgB_2 bulks and the volume of MgB_2 bulks. Finally, the microstructure of MgB_2 bulks were observed by SEM.

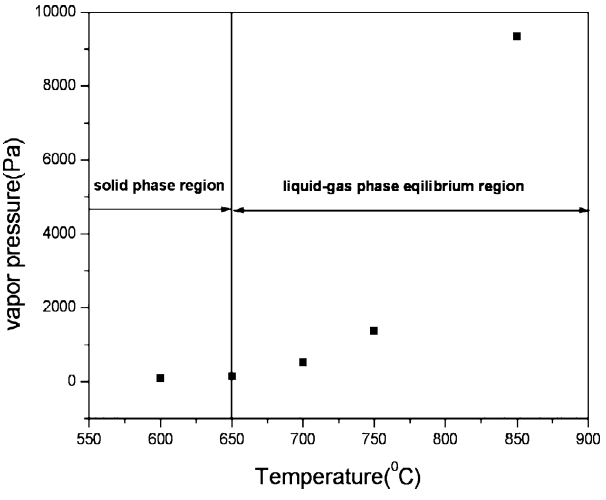

Figure 1 The vapor pressure of Mg vs. temperature in ambient pressure.

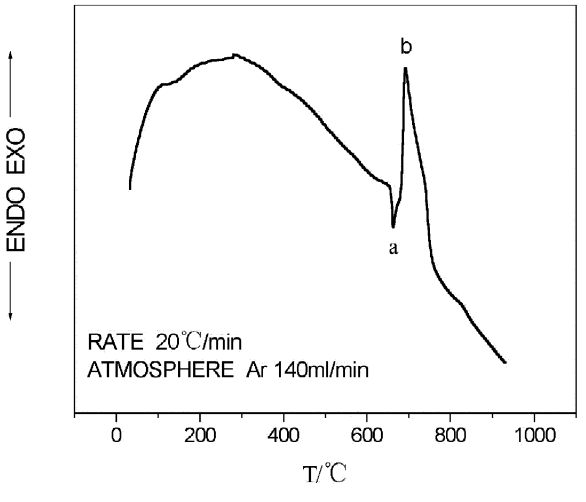

Figure 2 The DTA curve of mixture of Mg:B = 1:2.

3. Results and discussion

It is known that MgB_2 becomes very porous after high temperature sintering, which can be explained by the evaporation of Mg particles. Vapor pressure is a property constant of material, which denotes the gasification upetrend of solid materials. As for the phase transformation of solid-liquid and liquid-gas, the increase of vapor pressure means the much evaporation of solid materials. Fig. 1 shows the vapor pressure of Mg as a function of temperature in ambient pressure. There are solid-solid equilibrium region of Mg-B system under 650°C. The vapor pressure of Mg reaches 1383 Pa at 750°C, indicating event at this temperature a great deal of liquid Mg will turn into vapor. To the *in-situ* fabrication of MgB_2 wires and tapes, too much gasification of Mg will induce the loss of initial stoichiometric and more voids between Mg and metal substrate.

Fig. 2 illustrates the DTA curve for the composite of Mg:B = 1:2. The two peaks in the DTA curve represent the two reactions as following:

$$\mathrm{Mg(s)} \rightarrow \mathrm{Mg(I)}\ \text{(peak a)}$$

$$\mathrm{Mg(I)} + 2\mathrm{B(s)} \rightarrow \mathrm{MgB_2(s)}\ \text{(peak b)}$$

Here s denotes the solid phase and I is the liquid phase. Reaction (peak a) suggests that the solid state Mg becomes liquid state, while Reaction (peak b) shows the formation of MgB_2 phase. It is obviously that the combination reaction of MgB_2 (peak b) appears following the Mg melting reaction (peak a). The vapor pressure at Mg melting point 650°C is only 135 Pa, in which there will be less Mg vapor at this temperature. The liquid-solid reaction between Mg and B will improve the density of MgB_2. To study the decomposition of MgB_2 phase, the DTA analysis was employed and Fig. 3 illustrates the DTA curve for MgB_2 powder. It is clear that the reaction of MgB_2 decomposition starts at even as low as 810°C. So it is unnecessary to obtain the MgB_2 phase at high temperature. And It is known that MgB_2 becomes very porous after high temperature sintering, which can be explained by the evaporation of Mg particles.

The X-ray diffraction patterns of five MgB_2 pellets were presented in Fig. 4. It is clearly observed that the samples sintered at 600°C has MgB4 and MgO impurity phase and the samples sintered above 650°C have more MgO impurity as the increase of temperature. The samples fabricated at 650°C is single phase with a little MgO impurities. The results indicate that the

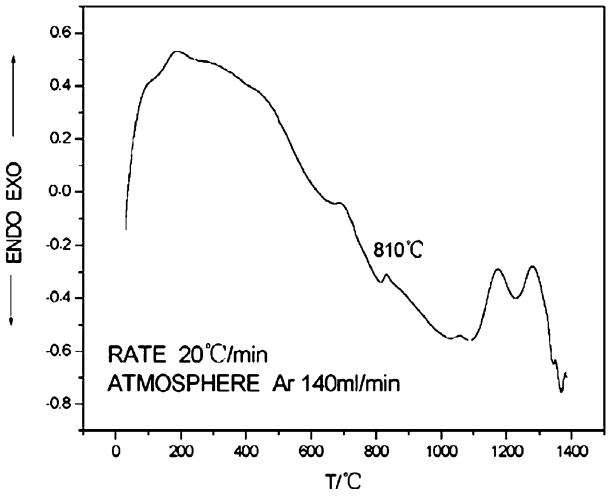

Figure 3 The DTA curve of MgB_2 powder.

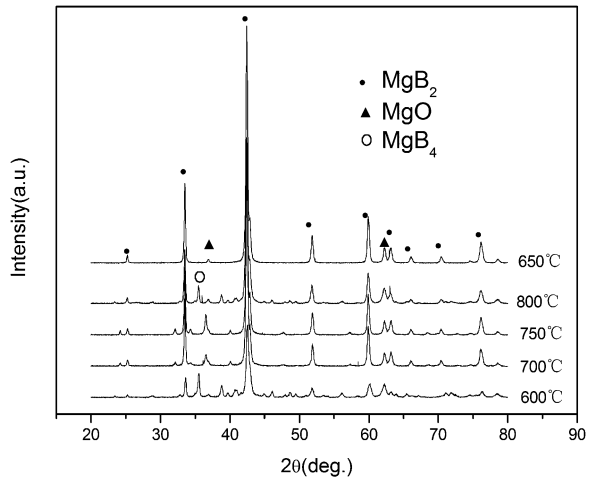

Figure 4 The XRD patterns of MgB_2 bulks synthesized at different temperature.

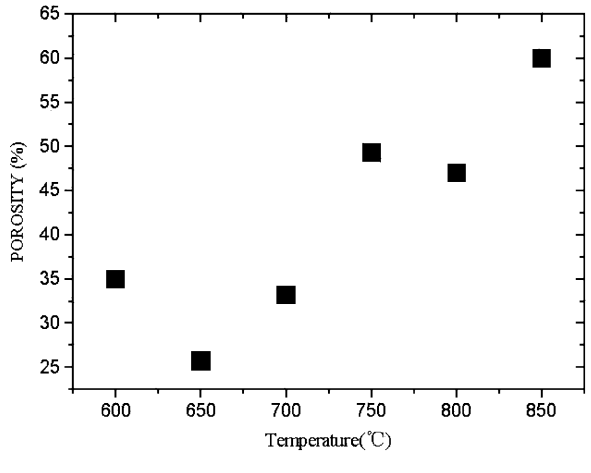

Figure 5 The porosity measurement results of MgB_2 bulks synthesized at different temperature.

diffuseness between Mg and B is not sufficient when the process temperature is under 650°C. On the other hand, the evaporation of Mg results in more voids in the MgB_2 samples prepared at temperature above 650°C. Fig. 5 shows the porosity of MgB_2 as a function of temperature. The data suggest that the samples sintered at 650°C has the smallest porosity in all samples. The mechanism of reaction between magnesium and boron below 650°C obeys the solid state diffuse principle. The solid state reaction between Mg particles and B particles can not induce porosity in bulk after the formation of MgB_2. So, there is certain porosity in the samples sintered below 650°C. The mechanism of reaction between magnesium and boron above 650°C obeys the solid-liquid-gas state principle. The amount of Mg gasification increases as increasing temperature. Meanwhile, the voids are induced by the evaporation of Mg particles. Thus, the porosity of MgB_2 material is higher after high temperature sintering. For the sample prepared at 650°C, the solid phase Mg will turn into liquid phase and the vapor poressure is very low. Thus, the reaction between Mg and B is a partial liquid-solid one and the Mg gasification is less. As expected, the density of this sample is the highest among all the samples. The results show the sintered temperature has a remarkable effect on the density of MgB_2 and indicated that the MgB_2 wires and tapes with high density can be prepared at 800°C or less in ambient pressure.

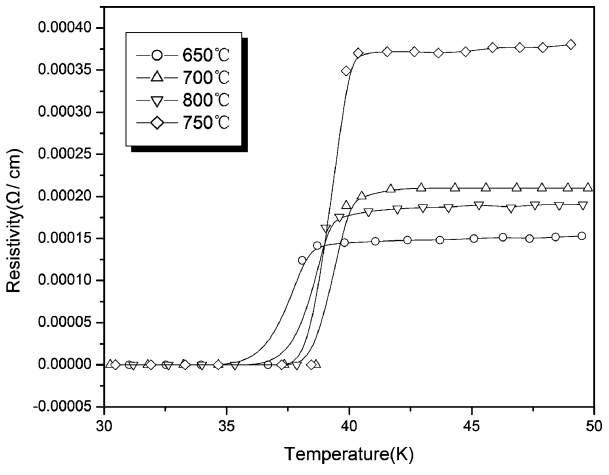

Figure 6 The critical transition temperature (T_c) of four MgB_2 bulks synthesized at 650, 700, 750 and 800°C.

The critical transition temperature (T_c) of MgB_2 bulks were shown in Fig. 6. There are four T_c transition curve and no resistive transition is shown for 600°C sample because there are too many non-superconducting phase present. The results indicates that the MgB_2 bulks synthesized at 700°C and 750°C with sharp transition have better superconducting properties. Fig. 7 shows that The SEM microstructure of MgB_2 bulks synthesized at 650, 700, 750 and 800°C. It can be seen that the effect of synthesis temperature on microstructure of MgB_2. The grain size of MgB_2 bulk synthesized at 750°C is smallest with a sphere shape in the four samples. It can be explained by that solid-liquid reaction mechanism of MgB_2 fabricated at 650 and 700°C which is favorable to growth of MgB_2 grain and thermal dynamic condition at 800°C or high which will induce increasing of MgB_2 grain size. And this result suggests that the thermal dynamic condition and appropriate vapor of Mg at 750°C can prevent the increase of MgB_2 grain. Considering it is useful to improve the flux prining properties that the small

grain with sphere shape in superconductor, this result indicated that the appropriate synthesis temperature for fabrication of wires and tapes will be about 750°C.

4. Conclusion

As the porosity in MgB_2 has important effect on superconducting properties, a method was developed to measure the porosity in MgB_2. A serious MgB_2 bulk samples were prepared at temperature range of 600–800°C at ambient pressure. The XRD and porosity measurement show the sample sintered at 650°C is single phase MgB_2 with highest density and less MgO phase. The experimental thermodynamic, SEM and T_c measurement results strongly suggest that the best feasible temperature range for fabrication MgB_2 with high density is 700–750°C. The results further indicate that the preparation of MgB_2 at the temperature range of 700–750°C will effectively reduce

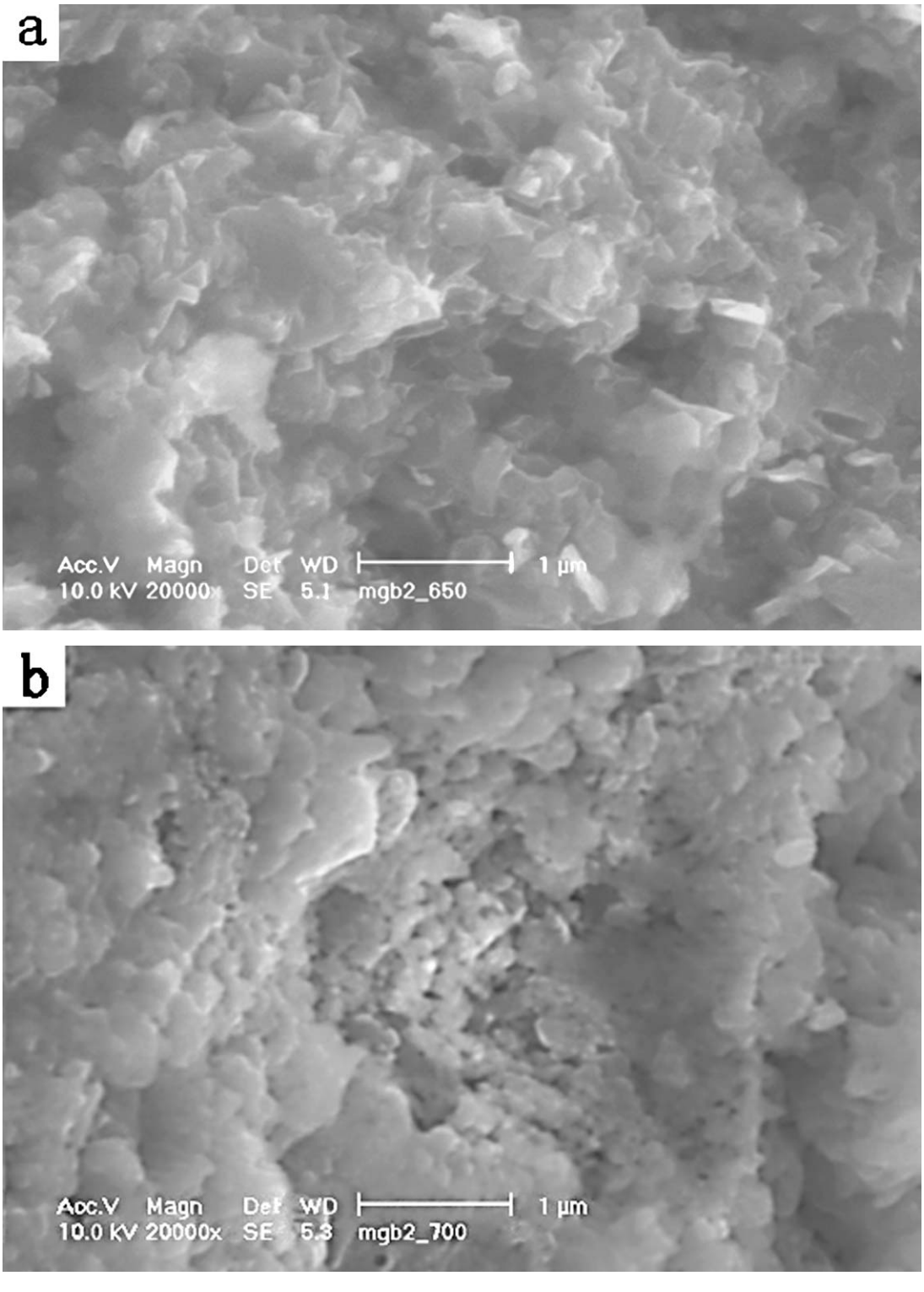

Figure 7 The SEM microstructure of MgB_2 bulks synthesized at different temperature: (a) at 650°C; (b) at 700°C; (c) at 750°C; and (d) at 800°C. (*Continued*)

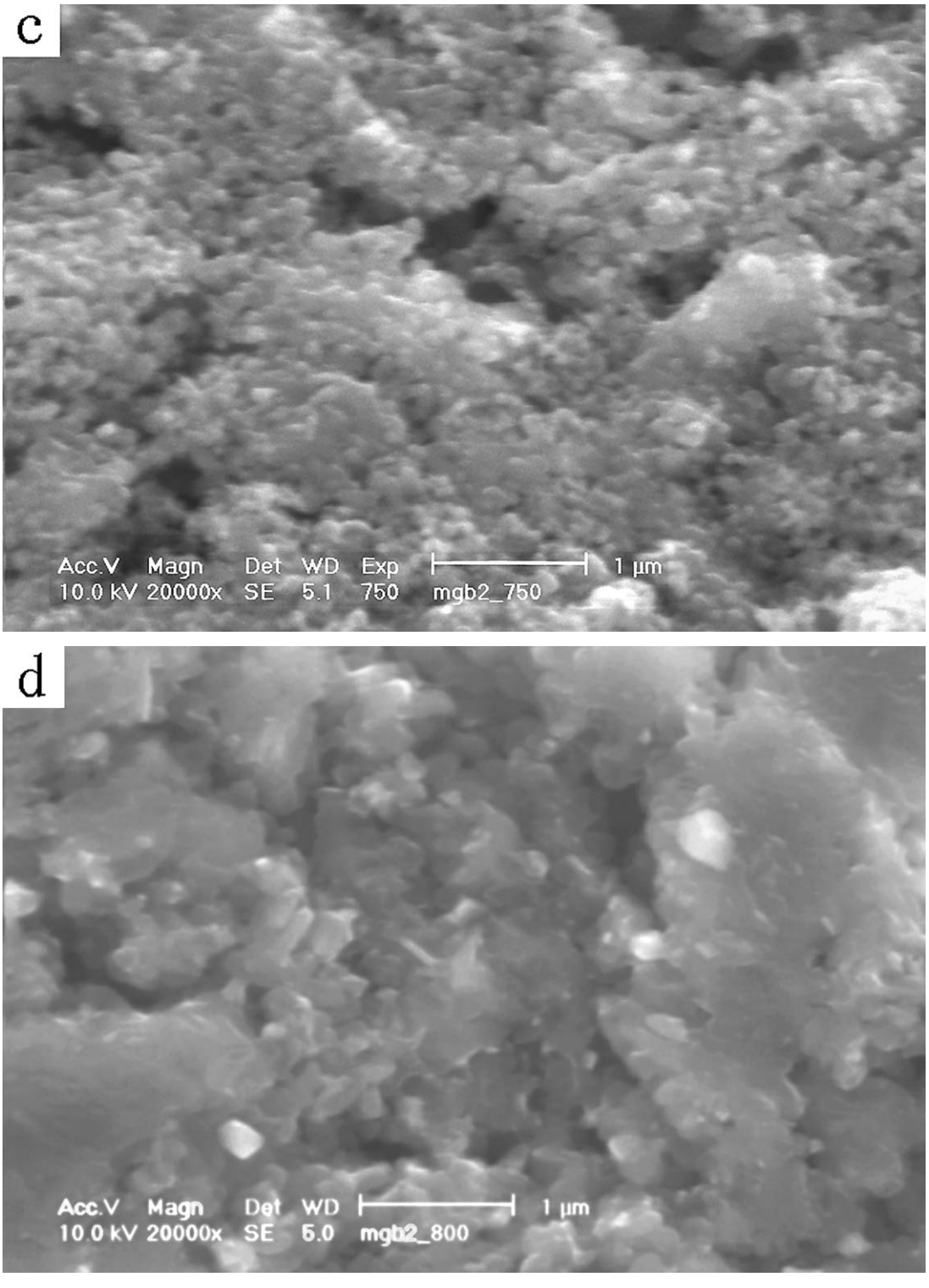

Figure 7 (*Continued*).

the porous of MgB_2 and improve the critical current density.

Acknowledgement

This research was supported by National Natural Science Founduation of China under contact No. 50172040.

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Received 14 January 2003
and accepted 26 February 2004