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Fabrication and growth mechanism of MgB_2 nanowires during reactive sintering

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Abstract

A direct synthesis route from Mg and B powders to crystalline MgB_2 nanowires was developed by reactive sintering: the sample was heated from room temperature to 994 K at a rate of 20 K/min and then cooled down at a rate of 40 K/min, according to the non-equilibrium conversion reaction theory. The prepared MgB_2 nanowires exhibit a uniform diameter of 50 nm. Both SEM and SQUID studies on the obtained nanowires suggest it has a high quality and a critical transition temperature comparable with that of an ideal one. A presumable mechanism for the process in the formation MgB_2 nanowires is also proposed, through which the formation of this special structure is considered to be connected with the preferable growth in several fixed crystal facets by assisting with liquid Mg melt.

Keywords: DTA; Nanowires; Superconductivity; Preferential growth

1. Introduction

With the highest critical transition temperature (T_c) of 39 K in non-copper-oxide compounds [1], MgB_2 has been intensively explored since 2001. In past years, many groups have put efforts into synthesizing various forms of the MgB_2 superconductor, such as bulk [2,3], thin films [4,5], and wires [6,7]. The influence of different morphology of MgB_2 on the corresponding superconductivity has attracted wide interest recently. However, there have been only a few reports on the synthesis and formation mechanism of MgB_2 nanostructure [8–10], which is very important for understanding basic science as well as the building blocks in new superconducting nanodevices. Wu et al. have successfully prepared MgB_2 nanowires through a two-step vapor transport and reaction process [11]. The other method synthesized by Ma et al. is direct pyrolysis from MgB_2 nanoparticles [12]. But the former methods are too complex to fabricate, and the superconducting transition temperature of the obtained sample is usually lower than that of the bulk material.

In this paper, a simple method, reactive sintering, was proposed to prepare MgB_2 nanowires, and the critical transition temperature, T_c, of the obtained crystalline MgB_2 nanowires was measured and compared to the ideal value. Additionally, the formation and growth mechanism of these nanowires is also discussed.

2. Experimental details

The starting materials used in this study were Mg (99% purity) and amorphous B powders (99% purity). After thoroughly mixing at the atomic ratio of 1:2, the powders were pressed into a cylindrical pellet with a diameter of 2 mm. The sample was annealed in an argon atmosphere in the differential thermal analysis (DTA), where the temperature was raised from room temperature to 994 K with a heating rate of 20 K/min. After reaching this programmed temperature, it was directly cooled down to room temperature at a rate of 40 K/min.

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The morphology and phase structure of the prepared sample was investigated by JSM-6700F field-emission scanning electron microscope (SEM), and X-ray diffraction (XRD) patterns were obtained by Rigaku D/max 2500 X-ray diffractometer with Cu Kα radiation.

In order to study the superconductivity property, measurements of resistivity versus temperature were performed by a conventional four-probe technique.

3. Results and discussion

3.1. DTA and XRD analyses

Since the sintering process was conducted in a differential thermal analyzer (DTA), the whole reaction could be recorded by the change of heat flow, which is very helpful in determining the highest sintering temperature. Fig. 1 shows the measured DTA curve as a function of sintering temperature up to 1073 K. It was found that the reaction of Mg and B powders started at about 803 K, and almost ended at about 994 K. The two exothermic peaks were found during the whole heating process, which was considered to be the reaction of Mg and B; the decalescence peak is still related to the melting process of Mg(s) → Mg(l). According to these results, 994 K was selected as the highest sintering temperature in the DTA instrument without holding at this temperature. Fig. 2 shows the XRD patterns of the prepared sample. The peaks mainly consisted of MgB_2 phase and with some trace of unreacted Mg metal, the existence of little MgO can be neglected. This suggested that a chemical reaction between Mg and B had been accomplished at this temperature, which coincides with the analysis of the DTA curve and, if given enough holding time, the residual Mg will completely convert into MgB_2.

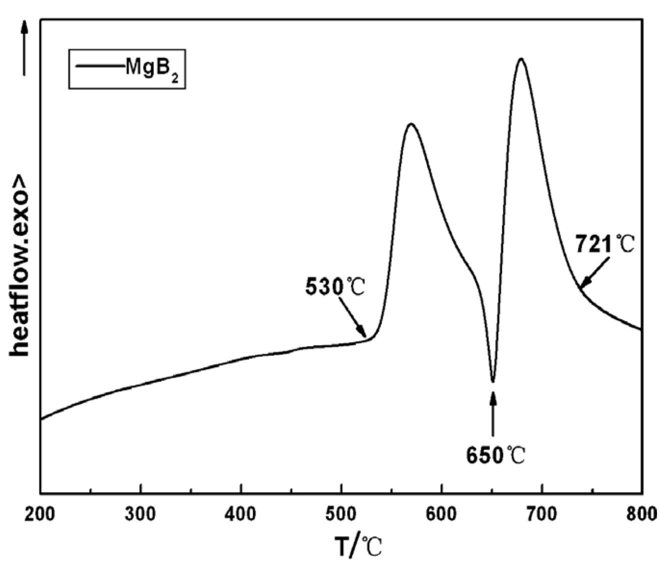

Fig. 1. DTA curve for the mixed powder of Mg:B = 1:2 with a heating rate of 20 K/min.

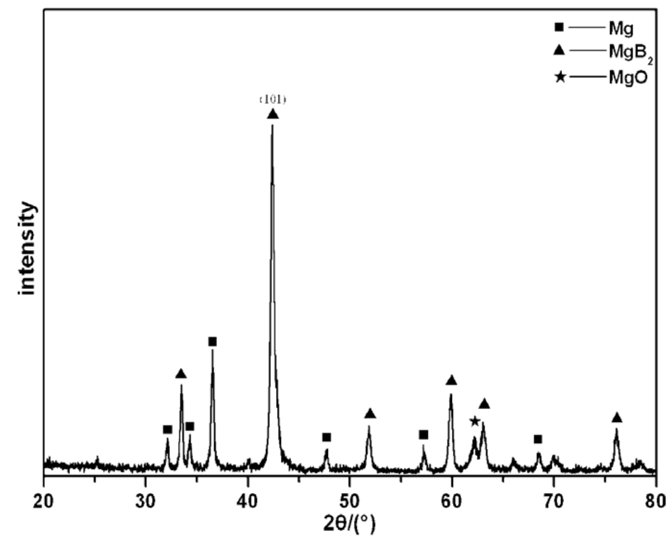

Fig. 2. XRD pattern of the as-prepared MgB_2 sample, the most intensive MgB_2 peak marked with a triangle is (1 0 1) plane.

3.2. Microstructural analyses

Fig. 3 illustrates the typical SEM images of the sintered MgB_2 samples. Abundant nanowires could be clearly observed. Most of them are tiny and have a uniform diameter of about 50 nm, at the same time, square-shaped structure is appeared at the end of the nanowire . It also seems that the axis in length usually stretches from inside to the surface, which is considered as the preferred orientation ladder. Such nano-structures are commonly observed in other areas of the sample, and they dominate the structure of the material.

Fig. 4 depicts the temperature-dependent electrical resistivity of MgB_2 nanowires. The arrow indicates the superconducting transition temperature of $T_c = 38.5$ K, the value of which nearly approaches the theoretical data, and it also means that unreacted Mg has little effect on T_c.

4. Growth mechanism of MgB_2 nanowire

As polycrystalline, MgB_2 particles need to reach its supersaturation in impregnant, while in this sample, Mg liquid just exhibits as this special kind of medium. The formation of MgB_2 particles derives from two ways. First, the remaining unreacted Mg exists in the form of liquid when the temperature rises to 923 K. These flowing liquids react so easily with B that there will be more MgB_2 particles to form than in the solid. Second, Mg is prone to vaporize following the increase of temperature. It has been reported that MgB_2 forms in a process of the diffusion of Mg vapor into an amorphous B matrix [10], so these gases can also react with B. The MgB_2 particles formed in these two ways both dissolve into Mg liquid and provide superfluous stuff. Then the formation process of MgB_2 nanowires is depicted as follows: