Applied Surface Science 261 (2012) 364–368

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Crystallization behavior of MgB_2 films fabricated on copper cathodes via electrochemical technique

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ARTICLE INFO

Article history:
Received 1 March 2012
Received in revised form 3 August 2012
Accepted 3 August 2012
Available online 10 August 2012

Keywords:
MgB_2 film
Crystallization behavior
Electrochemical technique

ABSTRACT

An electrochemical technique was devised and settled to prepare MgB_2 films on copper cathodes in $MgCl_2$–$Mg(BO_2)_2$–NaCl–KCl molten salts. X-ray diffraction and scanning probe microscopy were adopted to investigate the phase composition and elements distribution of sample. *R–T* curve of film was monitored through standard four-probe method. Transmission electron microscope and scanning electron microscope analysis were chosen to investigate the crystallization behavior and morphology of the films at different electrolytic temperatures. The results indicated that MgB_2 films were successfully fabricated on the copper cathodes, and the optimal electrolytic temperature was 601 °C. It was presumed that the non-conducting MgO impurities hindered continuous growth of MgB_2 grain, which may result in dendritic growth of MgB_2 grain.

1. Introduction

The discovery of superconductivity of MgB_2 has stimulated a considerable amount of theoretical and applied research [1,2]. To date, the most common processing techniques reported to prepare MgB_2 wires or tapes are based on the powder-in-tube (PIT) method [3–8]. The development of this conventional technique, however, is hindered in the industrial implementation due to its low scalability and high processing cost. Therefore, there are lots of opportunities to develop an alternative to make full use of the high potential of MgB_2 as a practical superconductor.

Yoshii et al. [9–12] devised a desirable alternative to the PIT technique named molten-salts electrochemical technique to prepare MgB_2 superconducting films on cathodes. The installations of the technique are very simple and the cost is also low, and it is a way to prepare MgB_2 films with a thickness of several micrometers on cathode with various size and shapes. Moreover, films prepared by this method possess excellent superconducting characteristics (H_{c2} (0) = 28*T*). However, MgB_2 films have only been fabricated on graphite and stainless steel cathodes via this method. In addition, the MgB_2 phase purity and crystallinity of films derived from this method are undesirable [9]. Furthermore, the distance between the two electrodes must be rigorous controlled, which increases the difficulties in the preparation process. Our group focus on preparation of MgB_2 films on novel cathode via molten-salts electrochemical technique, and the electrolytic cell has also been revised to decrease the difficulty to control the distance between the two electrodes [13]. However, the investigation is still in a primary stage: the optimal electrolytic temperature is uncertain and the crystallization behavior of MgB_2 phase has not been reported. These obstacles hinder the further investigation on MgB_2 films derived from electrochemical method.

In this paper, crystallization behavior of MgB_2 grain was investigated under different electrolytic temperatures. Morphology of the film was investigated to clarify the growth of film. The investigation is beneficial to comprehend the growth of MgB_2 films via electrochemical technique and enhance the properties of films.

2. Experimental

2.1. Preparation of MgB_2 films on copper cathode

Fig. 1 is a schematic diagram of an electrolytic cell. A graphite crucible was used as anode as well as an electrolyte container to decrease difficulty to adjust the distance between the two electrodes. The copper cathodes were insert in $MgCl_2$–$Mg(BO_2)_2$–NaCl–KCl electrolyte with a molar ratio of 10:2:5:5. The electrolysis was started by applying a constant dc voltage of 4 V between the two electrodes, and the detail experimental process was introduced elsewhere [13]. Electrolytic conditions of samples 1#–4# were listed in Table 1, and the electrolytic temperature was rigorously controlled to ensure that the temperature fluctuation was about ±2 °C. After the electrolytic

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http://dx.doi.org/10.1016/j.apsusc.2012.08.015

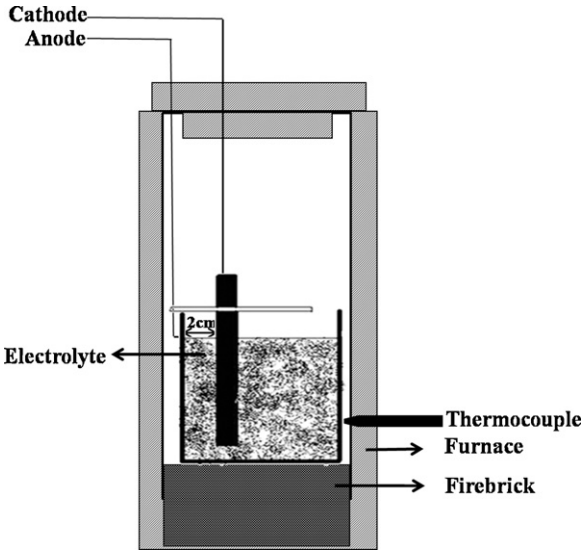

Fig. 1. Schematic diagram of an electrolytic cell.

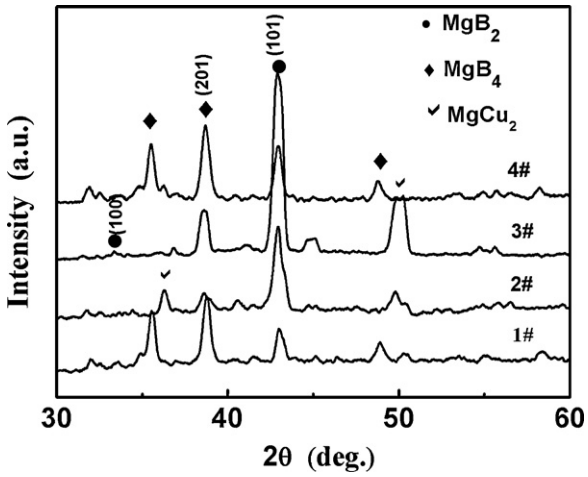

Fig. 2. XRD patterns of samples prepared on copper cathode. The setting electrolytic temperature of samples 1#–4# was set as 595 °C, 598 °C, 601 °C and 604 °C, respectively.

process, the cathode was pulled out of the electrolyte but still in the furnace to avoid the oxidation of film derived. After the furnace cooling down to room temperature, the film was taken out from the furnace, and the solidified electrolyte sticking to the film was washed off with dried methanol using an ultrasonic washer.

2.2. Characterization

X-ray diffraction (XRD) analysis (Cu Kα, scanning rate: 2°/min) and scanning probe microscopy (SPM) was used to investigate the phase composition and elements distribution of the films. Standard four-probe method was adopted to monitor the temperature dependence of resistance of the films. Transmission electron microscope (TEM) and scanning electron microscope (SEM) analysis were chosen to investigate the crystallization behavior and morphology of the films.

3. Results and discussion

The graphite crucible was applied as anode as well as an electrolyte container. In this way, the electrolytic cell was simplified, and the difficulty to adjust the distance between the two electrodes was decreased; and copper was used as cathode to prepare MgB_2 films, which may potentially be useful to the practical power application. In our former experiment [13], the desirable sintering temperature for MgB_2 films on copper cathodes was about 603 °C, and desirable sintering time was 1 h. However, since the temperature fluctuations varied in the range of ±4 °C at that time, influence of electrolytic temperature on phase purity and crystallinity of MgB_2 phase was not systematic and precisely. Therefore, different electrolytic temperatures were adopted to prepare MgB_2 films on copper cathodes, and the temperature fluctuation was rigorously controlled in the range of ±2 °C.

XRD patterns of samples derived at different conditions were shown in Fig. 2, and the electrolytic temperature of samples 1#–4# was 595 °C, 598 °C, 601 °C and 604 °C, respectively. According to standard JCPDS data, MgB_2 phase, MgB_4 phase can be found in all of the samples. In addition, a weak MgB_2 (1 0 0) peak can also be found in samples 3#. The full width at half maximum (FWHM) of MgB_2 (1 0 1) peak and the intensity ratio of MgB_2 (1 0 1) peak to MgB_4 (2 0 1) peak were listed in Table 2. It was shown that the intensity ratio of MgB_2 (1 0 1) peak to MgB_4 (2 0 1) peak for samples 1#–4# was 0.66, 3.95, 4.46 and 0.50, respectively. Besides, FWHM values of MgB_2 (1 0 1) peak for samples 1#–4# were 0.22°, 0.22°, 0.21° and 0.20°, respectively. It was interesting that some impurities peaks can be found at around 36°and 51° in samples 2# and 3#, which may be attributed to $MgCu_2$ phase. However, the peaks disappeared in sample 4#. Therefore, diffusion of Cu element increased with the increase of temperature from 595 °C to 601° C. As a result, Cu–Mg compound can be formed. Furthermore, $MgCu_2$ peaks shifted to larger angle with the increase of temperature, hinting the crystal structure change of Mg–Cu compounds, which was in accordance with results of Liang et al. [14]. When the temperature increased to 604 °C, most of Mg element lost owing to the high saturated vapor pressure, and little Mg–Cu compound can be found. It should be noted that diffraction peak of MgO impurity was fairly close to that of MgB_2 (1 0 1) peak, which may influence the intensity ratio calculation. Therefore, taken both the phase purity and crystallinity of MgB_2 phase into account, the desirable electrolytic temperature was 601 ± 2 °C (sample 3#) for the copper cathode.

Temperature dependence of resistance was monitored through standard four-probe method, as shown in Fig. 3. It was interesting that the transition temperature was about 50 K (in normal state the T_c of MgB_2 is around or below 40 K). In fact, in our previous study [13], according to *R–T* and *M–T* measurements, we found the superconducting transition takes place close to 50 K for MgB_2 films when the electrolytic temperature was around 603 °C. The increase of T_c by about 2 K in MgB_2 films was also found by Pogrebnyakov et al. when preparing MgB_2 films on SiC substrate, and the potential reason was attributed to the tensile strain in the MgB_2 films

Table 1
Electrolytic conditions of samples.

Samples	Temperature (°C)	Time (h)
1#	595 ± 2	1
2#	598 ± 2	1
3#	601 ± 2	1
4#	604 ± 2	1

Table 2
FWHM of MgB_2 (1 0 1) peak and the intensity ratio of MgB_2 (1 0 1) peak to MgB_4 (2 0 1) peak.

Samples	FWHM/°	Intensity ratio
1#	0.22	0.66
2#	0.22	3.95
3#	0.21	4.46
4#	0.20	0.50