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ORIGINAL PAPER

Electrochemical synthesis of magnesium borate whisker

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Abstract This study successfully synthesised magnesium borate ($Mg_2B_2O_5$) whiskers using a simpler electrochemical method and lower energy consumption compared with traditional methods. Metallic magnesium was anodised under low-voltage conditions in a borate solution containing ethanol/water mixtures and poisoning agents. The composition and morphology of the magnesium borate whiskers were determined by X-ray diffraction and scanning electron microscope measurements, respectively. The magnesium borate whiskers were 6–8 μm long, each with a diameter of 500 nm. The ratio of the length to the diameter ranges from 12:1 to 16:1. The average current efficiency was 72.6%.

Keywords Magnesium borate · Whisker · Anodise · Electrochemistry

1 Introduction

As a new type of functional material, magnesium borate ($Mg_2B_2O_5$) whisker is widely used in metal and alloy compounds [1, 2], polymers, composites and catalysts [3–5]. Several techniques have been developed to synthesise $Mg_2B_2O_5$, including the mechano-chemical method [6], the high temperature molten salt method [7], the microwave solid phase method [8], the sol–gel method [9], the hydrothermal precursor method [10], the chemical vapour deposition method [11, 12] and hydrothermal synthesis [13]. However, these methods have several disadvantages, including tedious treatment process, high temperature, high pressure, equipment complexity and high energy consumption. Furthermore, controlling whisker size and morphology remains challenging because accurate control of nucleation and growth process is difficult. Thus, synthesising $Mg_2B_2O_5$ whiskers is critical and requires continued research.

The present study reports a new method of electrochemically synthesising $Mg_2B_2O_5$ whiskers using a simple one-step approach. This is the first attempt to synthesise $Mg_2B_2O_5$ whiskers electrochemically with no template. This method only requires moderate room temperature and atmospheric pressure conditions; therefore, the process is simpler and has lower costs compared with traditional methods. Moreover, this method does not generate pollutants because the reactants are electrons.

2 Experimental part

2.1 Electrode pre-treatment

Titanium plates (60 × 10 × 1.5 mm) were used as cathodes. They were sanded with 120# sandpaper to remove the oxidised surface, etched in hydrochloric acid solution (15–25%), and later rinsed with distilled water.

Magnesium ribbons (100 × 10 × 2 mm, 99.9% purity) were used as anodes; they were pre-treated with boiling hydrochloric acid (10%) until an oxide film appeared, rinsed thoroughly with distilled water, polished with 120# sandpaper, sonicated in pure ethanol for 15–25 min, and finally air-dried.

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2.2 Preparation of $Mg_2B_2O_5$ whiskers

Magnesium ribbon and the titanium plate were used as the working electrode and counter electrode, respectively. The experiments were carried out at room temperature (20 ± 2 °C) in a one-compartment glass cell. The electrolyte consisted of ethanol/water mixtures (1:3), sodium chloride (0.01–0.2 mol L^{-1}), borate (0.2–1.5 mol L^{-1}) and a poisoning agent (0.1–0.3 mol L^{-1}). The voltage was controlled between 2 and 4 V. After 2 h, the magnesium ribbon with dense areas of $Mg_2B_2O_5$– whisker was moved into the oven, was dried at 140–150 °C, and was then cooled down at room temperature.

2.3 Characterisation of the whiskers

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/max-2500 diffractometer with Cu Kα radiation. Scanning electron microscope (SEM) images were acquired using JSM 26700F-type SEM.

3 Results and discussion

3.1 XRD results

Figure 1 shows the XRD pattern of as-prepared $Mg_2B_2O_5$–whiskers. The first three strong diffraction peaks could be indexed with lattice parameters of $a = 0.6155$ nm, $b = 0.9220$ nm, and $c = 0.3122$ nm. The data match well with the standard diffraction pattern of $Mg_2B_2O_5$ (JCPDS Card no: 15-0537).

The shape of the diffraction peaks suggests that the $Mg_2B_2O_5$ whiskers were well crystallised. The characteristic peaks at 2, 8, and 9 ($2\theta = 21.518°, 34.282°, 35.200°$, respectively) in the spectrum corresponded to the [−1 2 0], [210], and [0 2 1] crystal planes, respectively. The MgB_6O_{10} was also detected based on the characteristic peaks at 3 and 4 ($2\theta = 23.860°, 26.717°$, respectively).

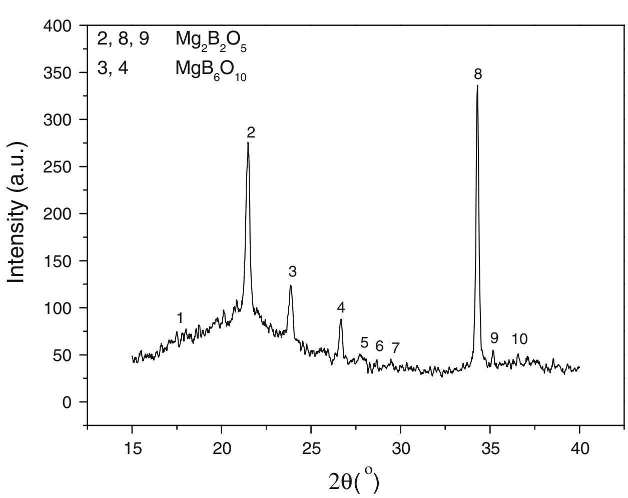

Fig. 1 XRD pattern of magnesium borate whiskers

Compared with standard peaks, the diffraction peaks of the sample shifted to the left, and the diffraction angle was lower than the standard angle, indicating that the parameters of the crystal lattice were increasing. The intensity of the peaks was inconsistent with the standard peaks because of the different orientation forces in the anode surface.

3.2 SEM results

At the beginning of anodisation, a visible black layer gradually formed within 1 h. After drying the samples in the oven at 200 °C, a large white area was observed on the magnesium surface. Figure 2 shows the typical morphology as imaged by SEM of the as-prepared magnesium borate whiskers arrays. The one-dimensional nanostructure consisting of a large quantity of whiskers is readily apparent.

Figure 2a shows typical morphologies of the magnesium borate whiskers, magnified 3,000 times in SEM. The white areas represent densely covered areas of magnesium borate nanowhiskers. From this, a surface coverage of about 60% can be estimated. The whiskers have a needle-tip shape with a tip diameter of 500 nm and an individual length of up to 6–8 μm. The SEM indicates that most oxidation products have uniform length and diameter. Multiple whiskers or bundles of whiskers grew in different directions from one nucleation root, which may have contained a cluster of nucleation seeds.

Figure 2b shows an anodised surface SEM picture magnified 1,000 times. The white areas represent densely packed whiskers. The remaining uncovered black areas are the surface of the magnesium. The figure shows that the magnesium borate whiskers are oriented perpendicular to the magnesium strip surface and uniformly cover the substrate with an estimated surface coverage of about 85%.

Figure 2c shows the SEM picture of the as-formed magnified 20,000 times. The whiskers have a needle-tip shape with an average tip diameter of 500 nm and an individual length of 6–8 μm. The ratio of the length to the diameter ranges from 12:1 to 16:1, which is in accordance with the definition of a whisker.

3.3 Electrode reaction process

According to the cluster shape and the growth mechanism of whiskers, a poison-induced mechanism [14] can be postulated in the formation of magnesium borate whiskers.

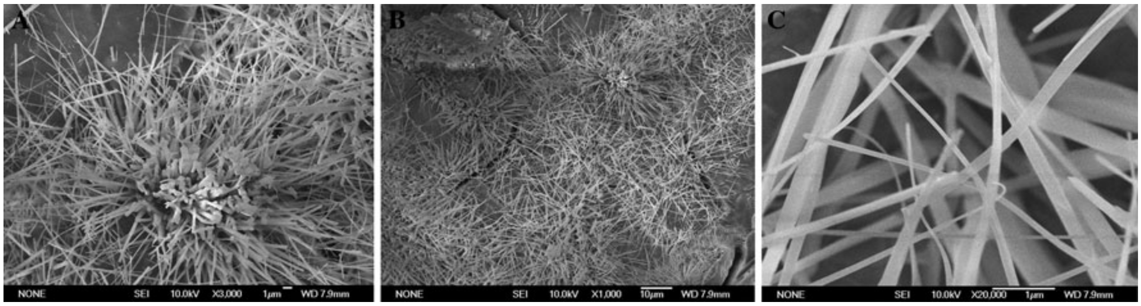

Fig. 2 **a** Morphology of $Mg_2B_2O_5$ whiskers with cluster shape under SEM (×3,000). **b** Morphology of $Mg_2B_2O_5$whiskers under SEM (×1,000). **c** Morphology of $Mg_2B_2O_5$whiskers under SEM (×20,000)

During the reaction, the poisoning agents (Polyvinyl alcohol) adsorbs in some crystal planes of magnesium borate crystal to reduce the activities of these planes, while other planes consistently grow to whiskers [15].

Released gas bubbles from the surface of either working or counter electrodes were observed during the electrolysis process, indicating the formation of O_2 and H_2, respectively.

The results demonstrate that the growth of whiskers is an electrochemical process that can be simply represented by the following two electrochemical half reactions:

$$\begin{aligned} \text{Anode}: \quad & Mg - 2e^- \rightleftharpoons Mg^{2+} \\ & 2Mg^{2+} + 2H_3BO_3 \rightleftharpoons Mg_2B_2O_5 + 4H^+ + H_2O \\ & 2H_2O - 4e^- \rightleftharpoons O_2\uparrow + 4H^+ \\ \text{Cathode}: \quad & 2H^+ + 2e^- \rightleftharpoons H_2\uparrow \end{aligned}$$

During this reaction, voltage can influence the morphology of the whiskers. No whiskers were generated from the electrochemical reaction when voltage was increased up to 10 v. Other elements such as temperature, current density, and electrolyte concentration can also influence the morphology of magnesium borate whiskers. Thus, obvious changes in the length and the diameter of the product indicate that the various factors used in this method are important. The magnesium borate whiskers were prepared without a template [16].

The current efficiency can be calculated by the equation expressed below:

$$\eta = (Q/Q_r) \times 100\% \quad (1)$$

$$Q = (m/M) \times zF \quad (2)$$

$$Q_r = It \quad (3)$$

where m is the mass of the product ($Mg_2B_2O_5$, g), M is the molecular weight of $Mg_2B_2O_5$ (g/mol), z is the number of electrons-transfer, F is the Faraday's constant 96500 (C/mol), I is the current intensity, t is the reaction time. The current efficiency of the reaction is about 72.6%.

4 Conclusions

Highly oriented magnesium borate whiskers can be directly synthesised using an electrochemical method in a boric acid solution containing sodium chloride, ethanol/water mixtures and poisoning agents at room temperature. XRD spectra demonstrate that the main product is $Mg_2B_2O_5$. The whiskers have a needle-tip shape with a tip diameter of about 500 nm and an individual length of 6–8 μm. The ratio of the length to the diameter is 12:1 to 16:1. Their average current efficiency is 72.6%. The growth mechanism of these magnesium borate whiskers is a poison-induced mechanism. This technique is eco-friendly, simple and inexpensive. It provides a new method to produce other types of whiskers.

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