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Short Communication

Anodized Oxidative Electrosynthesis of Magnesium Silicate Whiskers

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Magnesium silicate (Mg_2SiO_4) whiskers were synthesized by a simple anodized oxidative electrosynthesis method, which consumed lower energy and was easier to control than traditional methods. The Mg_2SiO_4 whiskers were deposited at the anode at a low voltage in a silicate solution containing poisoning agents. The composition and morphology of the Mg_2SiO_4 whiskers were determined by X-ray diffraction, scanning electron microscope, energy dispersive spectrometer and infrared spectrum analysis, respectively. The Mg_2SiO_4 whiskers were 5–6 μm long and 500 nm in diameter. The length-to-diameter ratio ranged from 10:1 to 12:1.

Keywords: Magnesium silicate; Whisker; Electrosynthesis; Anodic oxidation

1. INTRODUCTION

Magnesium silicate (Mg_2SiO_4) whiskers are gaining increased attention because these porous materials have a high specific area and specific breakout force. Mg_2SiO_4 whiskers have some important characteristics, such as excellent mechanical properties, high fracture strength, good compatibility, smoothness, chemical stability, and high heat resistance. Mg_2SiO_4 whiskers have potential applications in pharmaceutical intermediates, food additives, rubber fillers, deodorizers, and ceramics[1].

Whiskers can be prepared by the following methods. First is the mechanochemical method[2]. Second is the high-temperature molten salt method, which Li[3] used to synthesize magnesium borate whiskers 20–50 μm long and 1–2 μm in diameter. Third is the commonly used sol–gel method[4], which Cao[5] used to prepare nanomaterials 20 nm in average particle size by the homogeneous precipitation of alcosol, with magnesium chloride and boric acid as raw materials. Fourth is the

microwave solid-phase method, which Wang[6] used to synthesize pure and uniform magnesium borate whiskers tens of microns long. Fifth is Oxidation-Reduction Reaction，which Hashimoto[7] used to prepared Magnesium orthosilicate whiskers with long sides in a cross-sectional view from two to ten times as long as the short sides. Sixth is chemical vapor deposition[8,9]. Seventh and last is hydrothermal synthesis[10], which Xiang[11] used to prepare uniform magnesium borate whiskers 0.5–20 μm long and 10–90 nm in diameter, with a 10:200 aspect ratio and controllable morphology. All these methods have the disadvantages of tedious treatment, high pressure and temperature requirement, expensive equipment, as well as high energy consumption. Controlling the whisker size and morphology is also challenging because of the difficult accurate control of nucleation and growth. Thus, synthesizing Mg_2SiO_4 whiskers is critical and requires comprehensive research.

Reports on Mg_2SiO_4 whisker preparation using the abovementioned traditional methods are limited. This study presented a new method of electrochemically synthesizing Mg_2SiO_4 whiskers by anodic oxidation. Magnesium-tablet anodic-oxidized Mg^{2+}, Mg^{2+} and silicate in the electrolyte combined to generate Mg_2SiO_4. Most of the silicates did not dissolve in water, so Mg_2SiO_4 was deposited onto the anode surface. The current, voltage, and poisoning agent were adjusted to control crystal growth and ensure preferential adsorption of the poisoning agent on the spiral peripheral of the nuclei to facilitate slow growth. The subsequent rapid internal growth then led to whisker formation. This report was the first one on the template-free electrochemical synthesis of Mg_2SiO_4 whiskers by anode deposition. The method was performed at room temperature and atmospheric pressure, making the process simpler and less costly than traditional methods. Moreover, no pollutant was generated because the reactants were electrons.

2. EXPERIMENTAL

2.1. Electrode treatment

Titanium plates ($60 \times 10 \times 1.5$ mm^3) were used as cathodes. They were polished with #120 sandpaper to remove the oxidized surface, etched in hydrochloric acid solution (15wt.%–25wt.%), and rinsed with distilled water.

Magnesium ribbons ($100 \times 10 \times 2$ mm^3, 99.9% purity) were used as anodes. They were pretreated with boiling hydrochloric acid (10 wt.%) until an oxide film formed, thoroughly rinsed with distilled water, polished with #120 sandpaper, sonicated in pure ethanol for 15–25 min, and finally dried under ambient air conditions.

2.2. Preparation of Mg_2SiO_4 whiskers

The magnesium ribbons and titanium plates were used as the working and counter electrodes, respectively. The experiments were conducted at room temperature (20 ± 2 °C) in a one-compartment glass cell. Solid sodium silicate (2.0 g) and sodium chloride (0.5 g), both analytical reagent grade, were dissolved in 60 ml of an anhydrous methanol and water solution (1:3, v/v). Meanwhile, about 0.6 g of

solid polyvinyl alcohol (PVA; molecule weight = 1700) was dissolved by heating at 80 °C, and then 0.2 ml of this PVA melt was added to the above anhydrous methanol and water mixture. The voltage was controlled at 2.5 V. After 1 h, magnesium ribbons with dense areas of Mg_2SiO_4 whiskers were obtained, washed with distilled water, oven dried at 150 °C, and then cooled to room temperature. The Mg_2SiO_4 whiskers were stripped from the magnesium tablets with an efficiency of 36%.

2.3. Characterization of Mg_2SiO_4 whiskers

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/max-2500 diffractometer with CuKα radiation. Scanning electron microscopy (SEM) was performed using a JSM 26700F-type SEM system. Energy-dispersive spectrometry (EDS) was conducted using an America LEO438VP to determine the elemental composition. Infrared (IR) spectrum analysis was performed using a Nicolet 6700 Fourier-transform infrared system.

3. RESULTS AND DISCUSSION

3.1. XRD Results

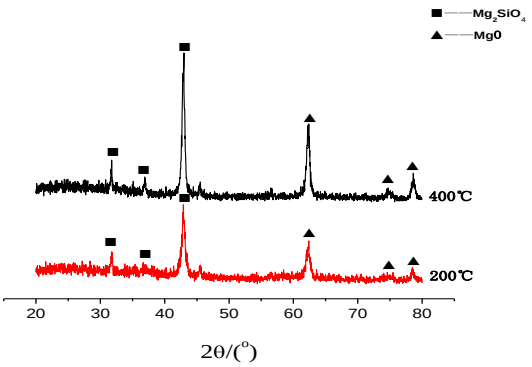

Figure 1. The XRD of Mg_2SiO_4 nanowhiskers

The XRD patterns of the as-prepared whiskers are shown in Fig. 1. The first three strong diffraction peaks were indexed to the lattice parameters a = 4.754 Å, b = 10.19 Å, and c = 5.979 Å. The data well matched the standard diffraction of Mg_2SiO_4 (JCPDS Card No. 84-1402).

The diffraction peaks suggested the Mg_2SiO_4 whiskers were well crystallized. The characteristic peaks numbered 1, 2, and 3 (2θ = 32.359°, 36.548°, and 41.812°, respectively) in the spectrum corresponded to the [130], [112], and [211] crystal planes, respectively. The strongest peak corresponded to the [211] crystal plane.

Compared with standard peaks, the diffraction peaks of the sample shifted to the left and the diffraction angle was lower than the standard one. The intensity of the peaks was inconsistent with

those of the standard peaks, which can be attributed to the different orientation forces on the anode surface.

3.2. SEM results

The SEM images of the white Mg_2SiO_4 whiskers prepared by anodic oxidation in the presence of poisoning agents are shown in Fig. 2. The whiskers were 5–6 μm long and 500 nm in diameter. The length-to-diameter ratio ranged from 10:1 to 12:1, consistent with the definition of whiskers. The whiskers had high purity have and evenly distributed dimensions. Meanwhile, Mg_2SiO_4 did not form whiskers in the absence of poisoning agents.

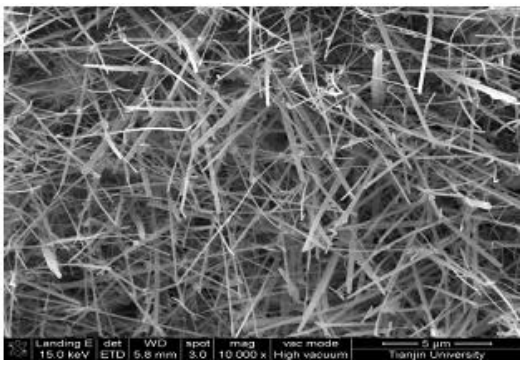

Figure 2. Typical SEM images of Mg_2SiO_4 nanowhiskers prepared in a Sodium silicate solution containing poisoning agents.

3.3 EDS Results

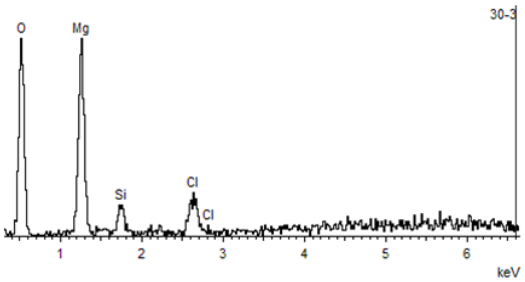

Figure 3. EDS spectra of Mg_2SiO_4 nanowhiskers

The energy-dispersive spectra of the Mg_2SiO_4 whiskers are shown in Fig.3. The products contained 71.80% Si, 21.04% O, and 3.17% Mg. This result indicated that the anodic oxidation product was a mixture of Mg_2SiO_4 and MgO, consistent with the XRD results.

3.4. IR Analysis

IR analysis was performed after drying the anodic oxidation product at 300 °C. Fig. 4 shows that for all samples, the diffraction peaks were at 3440, 1640, 1030, 1460, and 2360 cm^{-1}. The peak at 3440 cm^{-1} was associated with the constitution, surface, adsorbed, and pore water molecules in the samples. The peak at 1640 cm^{-1} was assigned to the bending vibration of H–O–H caused by surface, adsorbed, and pore water molecules. The strong and weak absorption peaks at 1030 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of the Si–O–Si bond[12], respectively. The strong absorption peaks at 1460 and 2360 cm^{-1} were associated with the bending vibration of Si–O, stretching vibration of Mg–O, and bending vibration of Si–O–Mg.

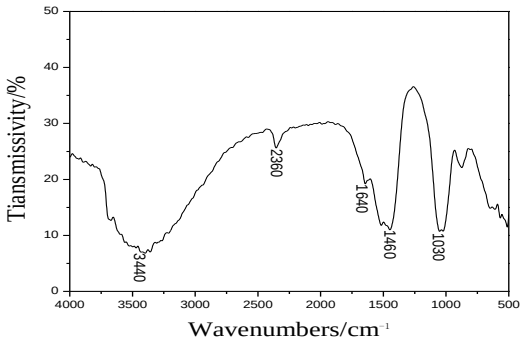

Figure 4. IR spectra of Mg_2SiO_4 nanowhiskers

3.5. Whisker growth mechanism

The electrochemical process of Mg_2SiO_4 whisker growth can be represented by the following electrochemical half-reactions:

Anode: $Mg - 2e^- = Mg^{2+}$

$2Mg^{2+} + 2SiO_3^{2-} = Mg_2SiO_4 + SiO_2$

$Mg^{2+} + O^{2-} = MgO$

Side effects: $2H_2O - 4e^- = O_2\uparrow + 4H^+$

Cathode: $2H^+ + 2e^- = H_2\uparrow$

The growth process of Mg_2SiO_4 whiskers was observed to occur in the following three stages: medium supersaturation, crystal nucleation, and whisker growth. The first stage is a prerequisite for whisker growth. Supersaturation of the medium can be maintained by two ways. One is by promoting the dissolution of magnesium electrode using sodium silicate as a cosolvent[13]. The other is by increasing the viscosity of the system using organic solvents such as ethanol to limit Mg^{2+} diffusion from the anode. Consequently, the anode near Mg^{2+} and silicate is supersaturated, which benefits crystal nucleation. The second stage is a thermodynamic phenomenon. It can be realized by controlling process parameters such as temperature, concentration, and current density, which induces rapid seeding and nuclei formation on the surface of the anode substrate, thereby contributing to Mg_2SiO_4

whisker growth. The third stage is a kinetic phenomenon. In this stage, the newly generated Mg_2SiO_4 continues to grow in the previously formed nuclei center along the axial and radial directions. To prevent multi-growth, small amounts of poisoning agents should be added to ensure preferential adsorption of these agents on the spiral peripheral of nuclei and facilitate slow growth. The subsequent rapid internal growth then leads to whisker formation.

4. CONCLUSIONS

Uniformly distributed Mg_2SiO_4 whiskers were prepared by an electrochemical method involving direct anodic oxidation. XRD patterns indicated good crystallinity, and the characteristic peaks of orthorhombic-system Mg_2SiO_4 were observed. EDS and IR analyses revealed that the product, comprised a mixture of Mg_2SiO_4 and MgO. SEM images showed that the morphology of the products met the definition of whiskers. The Mg_2SiO_4 whisker growth mechanism was discussed from the point of view of thermodynamics and kinetics. The proposed method is original to the best of our knowledge.

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References

1. S.Y. Chen, *Sichuan Chem Corro Contr,* 3(2006)3;
2. Y. Li, Z.Y. Fan, J.G. Lu. *Chem Mater,* 16(2004)2512;
3. H.Q. Li, S.F. Zhang, Z.Qi. *New Mater E,* 29(2001)16;
4. Y. Zeng, H.B.Yang, W.Y. Fu. *Mater Res B,* 43(2008)2239;
5. X.J. Cao, W.B. Zhu, C. Han. *Salt Chem Indus*, 36(2007)13;
6. H.D. Wang, Y. Li. *Salt Lake Res,* 6(1998)982102;
7. S. Hashimoto, A. Yamaguchi, *J. Amer. Ceram. Soc.,* 78 (1995) 1989;
8. R. Ma, Y. Bando, D. Golb. *Angew Chem Int Edit,* 42(2003) 1836;
9. J. Zhang, Z.Q. Li. *Mater Chem Phys*, 42(2006)195;
10. B. Jokić, M. Mitrić, V. Radmilović, S. Drmanić, R. Petrović and Dj. Janaćković, *Ceram. Intern.* 37 (2011) 167
11. X.T, Sun, L Xiang, W.C Zhu, Q Liu. *Cryst Res Tech,*43 (2008) 1057;
12. P. Fernandez-Ibancz, S. Malato. *Catal Today*, 54(1999) 195;
13. M.J. Zheng, L.D. Zhang, C.H. Li. *Appl Phys Let,* 79(2001)839;