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One-step synthesis of basic magnesium sulfate whiskers by atmospheric pressure reflux

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ABSTRACT

We have developed a one-step process for the synthesis of basic magnesium sulfate ($5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$, abbreviated as 513MOS) whiskers from $MgSO_4{\cdot}7H_2O$ and MgO by refluxing at atmospheric pressure. The process shows potential for the low-cost mass production of controlled-structure whiskers. Their 0.3–1.0 μm diameter and 40–80 μm length correspond to an aspect ratio of 40–260. The 513MOS whisker morphology is related closely to $MgSO_4$ concentration and reflux time. The optimized $MgSO_4$ concentration is 1.2–1.5 mol/L with a 25–30 h reflux time. X-ray diffractometry revealed that the *b*-axis is the predominant growth direction of the whiskers. Their growth mechanism is by the relatively slow liquid-phase deposition of Mg^{2+}, OH^-, and SO_4^{2-}. The long reaction time and high $MgSO_4$ concentration are conducive to the formation of 513MOS whiskers under gentle reaction conditions. Porous MgO whiskers with a fibrous structure were obtained after calcination of the 513MOS whiskers at 1020 °C.

Introduction

Magnesium oxysulfate whiskers have attracted attention because of their distinctive properties, such as low density, high elastic strength, high melting point and high modulus of rupture (Schierding & Deex, 1969; Yuan, Wong, & Wang, 1995). Basic magnesium sulfate ($5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$, abbreviated as 513MOS) whiskers are a type of magnesium oxysulfate whisker that can be used as a material reinforcing agent, a flame retardant for wooden materials, and a composite material additive for rubber and ceramics (Lu et al., 2004, 2006; Wei, Qi, Ma, & Bao, 2002). S-doped nanomesh graphene could be synthesized using calcined porous 513MOS whiskers as templates (Ma, Ning, Sun, Pu, & Gao, 2014). 513MOS whiskers are usually synthesized by hydrothermal processes (Ding et al., 2000; Gao, Li, Feng, Lu, & Liu, 2010; Li, Xiang, & Jin, 2006; Sun & Xiang, 2008; Xiang, Liu, Li, & Jin, 2004; Zhu, Yue, Gao, & Xia, 2003), which requires expensive equipment and is high-risk because of the elevated temperature and pressure, especially for mass production on an industrial scale. We present a simple one-step synthesis of 513MOS without hydrothermal treatment, which is promising for the mass production of 513MOS whiskers with well-controlled structure at low cost. The effects of $MgSO_4$ solution concentration and reflux time on the 513MOS whisker morphology were investigated to obtain optimized synthesis conditions. The growth mechanism of the 513MOS whiskers is also discussed in detail.

Experimental

513MOS whisker synthesis

Commercial MgO powder (Sinopharm Chemical Reagent Beijing Co. Ltd.) and $MgSO_4{\cdot}7H_2O$ (Tianjin Fuchen Chemical Reagents Factory, China) of analytic purity were used to synthesize 513MOS whiskers. In a typical synthesis, 4.00 g MgO powder was added to 300 mL $MgSO_4$ solution (0.3–1.5 mol/L) with intense agitation. The obtained slurry was transferred to a flask equipped with a water-cooled condenser, and refluxed at ~100 °C for 5–30 h. After cooling to room temperature, the suspensions were filtered and rinsed with deionized water and ethanol, and dried in an oven at 80 °C overnight to obtain the final product. Synthesis was conducted with different $MgSO_4$ concentrations and reflux times to optimize the process. The solid product yield (Y) is defined as:

$$Y = \frac{m_2}{\frac{m_1}{5M_1}M_2},$$

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where m_1 and m_2 are the MgO and solid product masses, respectively, and M_1 and M_2 are the molecular weights of MgO and 513MOS, respectively.

Characterization

The synthesized whisker products were characterized by scanning electron microscopy (SEM, Quanta 200F, USA), transmission electron microscopy (TEM, JEM2100, JEOL Ltd., Japan), X-ray powder diffractometry (XRD, D8 Advance, Bruker, Germany), thermogravimetric analysis (TGA, STA409PC, Netzsch, Germany) and Brunauer–Emmett–Teller surface area measurements (ASAP 2020, Micromeritics, USA).

Results and discussion

Reflux synthesis of 513MOS whiskers

Fig. 1a–c shows SEM images of the whiskers produced by typical reflux synthesis. The whiskers have a 0.3–1.0 μm diameter and 40–80 μm length, which corresponds to an aspect ratio of 40–260. The selected area electron diffraction (SAED) pattern (Fig. 1d) on the edge of a whisker (the inset of Fig. 1d) consists of intermittent rings, which can be indexed to the interplanar spacings of $5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$. The intermittent rings indicate that the whiskers have a single crystal structure. Most peaks in the XRD pattern of the as-produced whiskers (Fig. 2a) can be indexed to the orthorhombic structure of $5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$ (powder diffraction file No. 07-0415) and the remaining weak peaks correspond to the small amount of $Mg(OH)_2$ that exists in the products. Therefore, the products were confirmed to be 513MOS whiskers. The mass loss from 200–350 °C in the TGA curve of the as-prepared 513MOS whiskers (Fig. 2b) is attributed to the release of crystallization water (8.0% loss, ~$2.5H_2O$), and the mass loss from 350–585 °C corresponds to the release of residual crystallization water and the dehydration of $Mg(OH)_2$ (20.2% loss, ~$5.5H_2O$) (Kang & Lee, 2014; Xiang et al., 2004). The final mass loss between 850 °C and 1020 °C is ascribed to the release of SO_3 (15.9%) by the decomposition of SO_4^{2-}. The three mass losses are close to the related theoretical mass losses (9.7%, 21.3%, and 17.2%), which indicates a high purity of the as-prepared 513MOS.

Effect of reflux time and mechanism for whisker growth

In the study of reflux time, the $MgSO_4$ concentration was fixed at 1.5 mol/L. Fig. 3 shows the product morphology prepared using different reflux times (5–30 h). Only clusters and no whiskers formed for a reflux time of 5 h (Fig. 3a). The amount of clusters decreased and the amount of whiskers increased with increasing reflux time (Fig. 3b–f), until smooth whiskers with minimal impurities were obtained at 25–30 h (Fig. 3e and f). XRD patterns (Fig. 4a) show that the clusters were $Mg(OH)_2$, which was converted gradually to 513MOS whiskers with increasing reflux time. The solid product yield increased gradually with increasing reflux time and a maximum yield was obtained after 25 h (Fig. 4b). Consequently, the optimized reflux time was 25–30 h. Most of the XRD peaks (201, 202, 203, 401, 402, and 601) are attributed to (h 0 l) planes. As a result, the b-axis is the preferential growth direction of the 513MOS whiskers (Sun, Shi, Xiang, & Zhu, 2008). The a, b, and c crystallographic parameters for orthorhombic 513MOS whisker synthesis as calculated from $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$ (where d represents the interplanar spacing) are 1.594, 0.311, and 1.338 nm, respectively, which indicates that the 513MOS whiskers grow preferentially along the b-axis.

The growth mechanism of the 513MOS whiskers can be expressed by (Liu, Xiang, & Jin, 2004):

$$MgO + H_2O \leftrightharpoons Mg(OH)_2(s) \leftrightharpoons Mg(OH)_2(l) \leftrightharpoons Mg^{2+} + 2OH^- \quad (1)$$

$$6Mg^{2+} + 10OH^- + SO_4^{2-} + 3H_2O \rightarrow 5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O \quad (2)$$

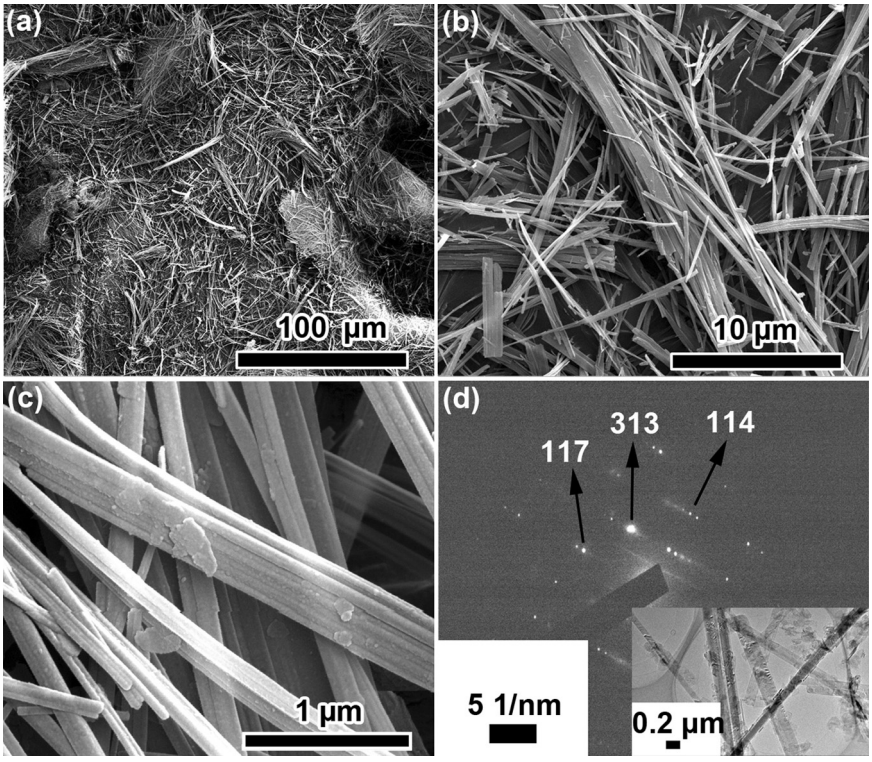

Fig. 1. (a)–(c) SEM images, (d) TEM image and SAED pattern of 513MOS whiskers produced by reflux synthesis.

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