J MATER SCI **41** (2006) 1345–1348

Hydrothermal formation of magnesium oxysulfate whiskers in the presence of ethylenediaminetetraacetic acid

J. LI, L. XIANG*, Y. JIN
Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China
E-mail: xianglan@flotu.org

An advanced method has been developed to synthesis magnesium oxysulfate hydrate ($5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$, abbreviated as 513MOS) whiskers via co-precipitation-hydrothermal reaction route, using $MgSO_4$ and NaOH as the reactants. $Mg(OH)_2$ slurry synthesized at room temperature was treated in $MgSO_4$ hydrothermal solution. 513MOS whiskers co-existed with the sector-like whiskers were formed after hydrothermal treatment at 200°C for 2.0 h. The presence of ethylenediaminetetraacetic acid (EDTA) in hydrothermal treatment inhibited the formation of the sector-like whiskers, producing 513MOS whiskers with perfect morphology (50–80 μm in length and 0.2–0.6 μm in diameter). Thermodynamic calculation results indicated that the addition of EDTA was favorable for the dissolution of $Mg(OH)_2$ and the homogeneous precipitation of 513MOS owing to the complex interaction between EDTA and Mg^{2+}. XRD analysis showed that 513MOS whiskers belonged to the orthorhombic structure ($a = 15.94$ Å, $b = 3.11$ Å, $c = 13.38$ Å) and b-axis was the predominant growth direction.

1. Introduction

Whiskers are filamentary single crystals with aspect ratios greater than 10:1. They are remarkable for their high strength which can approach the theoretical tensile strength of the material. Ceramic whiskers are, therefore, attractive materials for fiber reinforcement of ceramic composites for high temperature and stress applications [1–5]. In recent years the synthesis of MOS compounds, esp. 513MOS whiskers has become an attractive subject of numerous investigations in the ceramic field because 513MOS whiskers were shown good strength for building and plastic materials [6–13]. In spite of the fact that the hydrothermal synthesis of 513MOS whiskers has been studied by a lot of researchers, some problems such as the co-existence of the sector-like compounds and the low concentration of reactants still need to be solved to promote its commercial application.

In this paper, an advanced method has been developed to synthesis 513MOS whiskers via co-precipitation-hydrothermal reaction route, using concentrated $MgSO_4$ and NaOH aqueous solutions as the reactants and EDTA as the modification agent. The influence of EDTA on the morphology and structure of 513MOS whiskers were investigated, the corresponding reaction mechanism of EDTA was studied via the thermodynamic equilibrium calculation of $MgSO_4$-NaOH-EDTA aqueous system at elevated temperatures.

2. Experimental

2.1. Hydrothermal synthesis of $5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$ whiskers

Commercial NaOH, $MgSO_4{\cdot}7H_2O$ and EDTA reagents with an analytical grade (Beijing Chemical Regent Factory, China) were used in the experiment. For the preparation of whiskers, 10–20 ml of NaOH solution (2.5–4.5 $mol{\cdot}l^{-1}$) was dropped into 30–40 ml of $MgSO_4$ solution (1.6–2.5 $mol{\cdot}l^{-1}$) at room temperature. The slurry was then transferred to a Teflon-lined stainless steel autoclave with an inner volume of 80 cm^3 and kept stirred (200 min^{-1}). The autoclave was heated (5°C.min^{-1}) gradually to 200°C and then maintained the temperature in

*Author to whom all correspondence should be addressed.
0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-7339-4

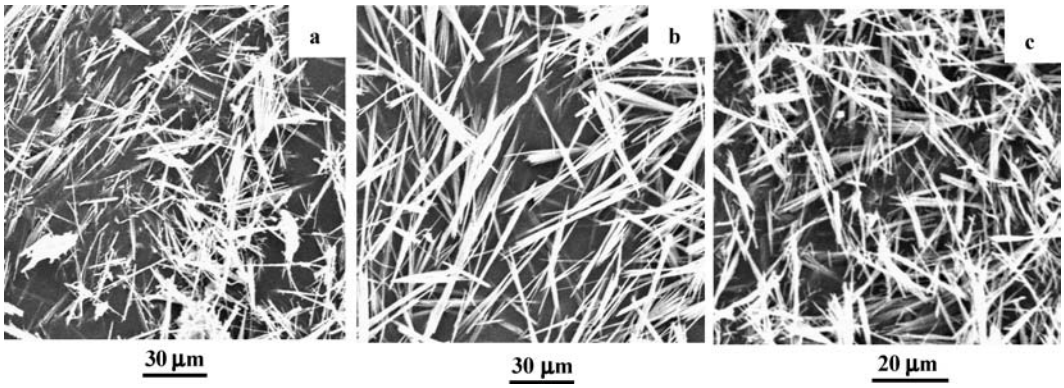

Figure 1 Morphology of hydrothermal products formed in the absence of EDTA Hydrothermal reaction time (hours): a-1.0, b-2.0, c-4.0.

isothermal conditions for 1–2 h. In the contrast experiment, 0.02 mol·l^{-1} EDTA was added into the slurry formed at room temperature to investigate its influence on the characteristics of hydrothermal product. After hydrothermal treatment, the autoclave was cooled down to room temperature naturally, the resulting suspensions were filtrated and the solids were washed several times with distilled water. Finally, the hydrothermal products were dried at 105°C for 12 h and stored in a desiccator.

2.2. Analyses

The morphology of the particles was examined with a scanning electron microscope (SEM, Model JSM-6301, JEOL, Japan) and transmission electron microscope (TEM, Model JEM-200CX, JEOL, Japan). Powder X-ray diffraction (XRD, Model D/max-RB, Rigaku, Japan) patterns of the samples were obtained using nickel-filtered Cu K_α radiation. The reference substance was alumina. Thermo-gravimetric analyzer (TGA, Model 2050, Beijing Optical Products Co., Ltd., China) was used to identify the thermal behavior of the hydrothermal product. The sample was heated under the air atmosphere from ambient to 1200°C at a heating rate of 20°C min^{-1}. The concentration of the total soluble Mg in the solution was detected with EDTA titration method.

3. Results and discussion

3.1. Hydrothermal formation of 513MOS whiskers

Figs 1 and 2 shows the morphology and structure of the hydrothermal products formed in the absence of EDTA, the initial $MgSO_4$:NaOH molar ratio was kept as 3:1. Fine whiskers with a diameters of about 0.2 μm and a length of 30 to 50 μm were formed (Fig. 1a) after 1 h of hydrothermal reaction, some un-regular particles were also observed; bigger whiskers with a diameter of 0.2 to 0.5 μm and a length of 50–80 μm were formed after 2 h of hydrothermal reaction (Fig. 1b);

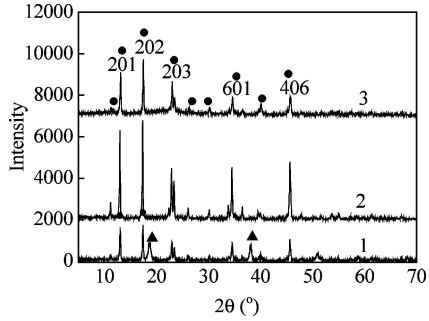

Figure 2. XRD patterns of hydrothermal products formed in the absence of EDTA Hydrothermal reaction time (h): 1-1.0, 2-2.0, 3-4.0; •: 513MOS: $Mg(OH)_2$.

the further prolongation of the reaction time to 4 h led to decrease of the whisker sizes due to the re-solving of the whiskers (Fig. 1c).

XRD analysis results (Fig. 2) indicated that both of $Mg(OH)_2$ and 513MOS phases were detected in the sample with 1 h of reaction; $Mg(OH)_2$ phase disappeared after 2 h of reaction and the intensity of XRD peaks for 513MOS phase decreased gradually if the reaction time was longer than 2 h. The crystallographic parameters for the orthorhombic 513MOS crystal were as follows: a = 15.94 Å, b = 3.11 Å, c = 13.38 Å, Z = 1. The comparatively stronger strength of (201), (202), (203) and (406) in all of the samples indicated that the growth direction of crystal was parallel to y axis.

It was noticed that the sector-like whiskers were detected in all of the samples. The typical morphology of the sector-like whiskers was shown in Fig. 3. The energy spectrum analysis of the selected areas showed that the composition of the sector-like whiskers at the intersection point and the main body was different from each other. As shown in Table I, no S element was detected at the intersection point, the corresponding ratio of O and Mg atoms (2.8:1) was a little higher than the theoretical value (2:1) of $Mg(OH)_2$, which may be connected with the existing of crystal water at hydrothermal condition. The atomic ratio

TABLE I Composition of the sector-like whiskers

Element	Atomic content at the whisker (%)	Atomic content at the intersection (%)
O	70	74
Mg	26	26
S	4	0

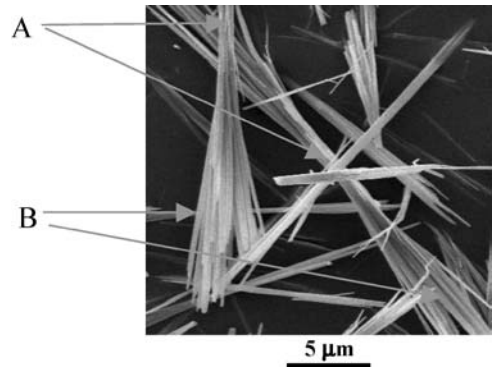

Figure 3 Morphology of the sector-like whiskers. Hydrothermal reaction time (hours): 2.0. A. Intersection point B. Sector-like whisker.

of O, Mg and S atoms was 17.5:6.5:1, quite similar with the theoretical values (15:6:1) of 513MOS compound.

It was deduced from the above experimental phenomena that the sector-like whiskers may be formed via the following route: some of the 513MOS crystals may grow on the surface of $Mg(OH)_2$ nucleates, part of the 513MOS whiskers shared the same basis and extended in different directions.

Fig. 4 shows the morphology of 513MOS whiskers in the presence of 0.02 mol·l^{-1} EDTA. The presence of EDTA prevented the existence of the sector-like whiskers, producing 513MOS whiskers with perfect morphology (50–80 μm in length and 0.2–0.6 μm in diameter). The role of EDTA was discussed further in the following part from the viewpoint of thermodynamics.

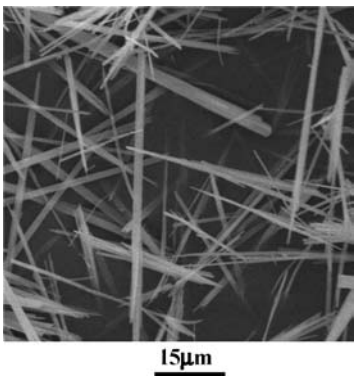

Figure 4 Morphology of 513MOS whiskers in the presence of EDTA. Hydrothermal reaction time: 2 h.

3.2. Effect of EDTA on the equilibrium

The following equilibrium reactions existed in the $MgSO_4$-Na_2SO_4-NaOH-EDTA aqueous system:

$$Mg(OH)_2(a) \leftrightarrow Mg^{2+}+2OH^- \quad (1)$$

$$Mg(OH)_2(a) \leftrightarrow MgOH^+ + OH^- \quad (2)$$

$$H_4Y \leftrightarrow H^+ + H_3Y^- \quad (3)$$

$$H_3Y^- \leftrightarrow H^+ + H_2Y^{2-} \quad (4)$$

$$H_2Y^{2-} \leftrightarrow H^+ + HY^{3-} \quad (5)$$

$$HY^{3-} \leftrightarrow H^+ + Y^{4-} \quad (6)$$

$$MgY^{2-} \leftrightarrow Mg^{2+} + Y^{4-} \quad (7)$$

$$6Mg^{2+} + SO_4{}^{2-} + 10OH^- + 3H_2O \rightarrow 5Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O \quad (8)$$

The variation of the equilibrium constants of reactions (1)–(7) with temperature was listed in Fig. 5. The simulation results for the activities of the total soluble Mg ion which was the summery of Mg^{2+}, $MgOH^+$ and $Mg(OH)_2(a)$, the free Mg^{2+} and OH^- ions at varying temperatures were shown in Figs 6

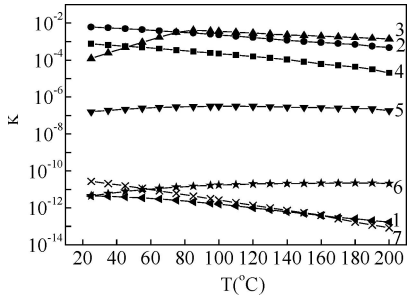

Figure 5 Equilibrium constants of reactions (1)–(7).

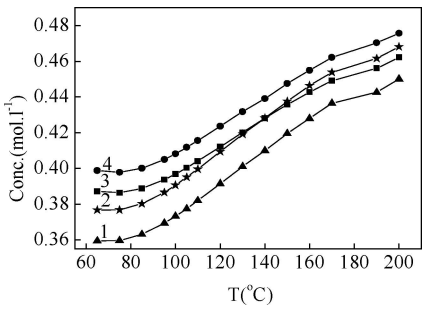

Figure 6 Variation of soluble Mg conc. with T1-Mg^{2+} without EDTA, 2-Mg^{2+} with EDTA, 3-total soluble Mg without EDTA, 4- total soluble Mg with EDTA.

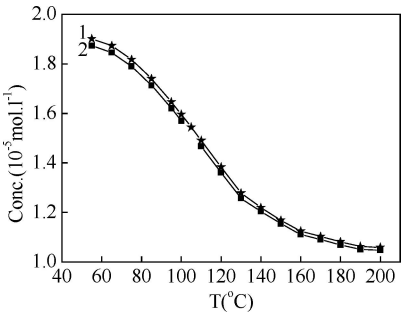

Figure 7 Variation of OH conc. with temperature in the absence (1) and presence (2) of EDTA.

and 7. The initial concentrations of $MgSO_4$, NaOH, Na_2SO_4 and EDTA were 0.45 mol·l^{-1}, 1.35 mol·l^{-1} and 0.02 mol·l^{-1}, respectively, the same as those in the slurry formed at room temperature. All of the calculation work was carried out by means of the commercial OLI software[14].

The data in Figs 5–7 shows that both of the increase of temperature and the presence of EDTA can accelerate the complex interaction between Mg^{2+} and EDTA, leading to the increase of the concentrations of the total soluble Mg ion and the free Mg^{2+} ion, which were favorable for the dissolution of $Mg(OH)_2$ and the homogeneous precipitation of 513MOS. Meanwhile the addition of EDTA showed little influence on the concentration of OH^- ion. As shown in Fig. 6, the theoretical concentrations of the total soluble Mg at 200°C in the presence and absence of EDTA were 0.476 mol·l^{-1} and 0.463 mol·l^{-1}, respectively, which were quite consistent with the experimental results (0.487 mol·l^{-1} in the presence of EDTA and 0.472 mol·l^{-1} in the absence of EDTA). The relative error between the practical and the theoretical results was less than 2.31%.

4. Conclusion

513MOS whiskers co-existed with the sector-like whiskers were formed after hydrothermal treatment of the slurry formed by mixing $MgSO_4$ and NaOH at room temperature. The formation of the sector-like structure may connect with the growth of 513MOS whiskers on the surface of $Mg(OH)_2$ nucleates. The addition of EDTA in hydrothermal conditions led to the increase of the soluble Mg ions which was favorable for the dissolution of $Mg(OH)_2$ and the formation of 513MOS whiskers with perfect morphology.

References

1 P. CHEANG and K.A. KHOR, *Mater. Sci. Techn. A* **345**(1/2) (2003) 47.
2 G. ONDREJ, H. ELENA, B. OLGA and L. PETER, *Polym. Degrad. and Stab.*, **64** (1999) 59.
3 U. HIPPI, J. MATTILA, M. KORHONEN and J. SEPPALA, *Polymer*, **44** (2003) 1193.
4 R. M. BAGWELLL and R. C. WETHERHOLD, *Mater. Sci. Eng.: A* **361** (2003) 294.
5 D. D. L. CHUNG, *Carbon* **39** (2001) 1119.
6 K. UENO, T. AKAGAWA and K. OBANA, United States Patent 4997871 (1991).
7 S. OTAKA, T. MATAUNAMI and Y. TASAKA, United States Patent 5326548, (1994).
8 T. YUE, S.Y. GAO, L.X. ZHU, S.P. XIA and K. B. YU, *J. Mol. Struct.*, **616** (2002) 247.
9 T. YUE, S. Y. GAO, L. X. ZHU, B. WANG and S. P. XIA, *Chinese J. Inorg. Chem.* **18** (2002) 313.
10 Z.Q. WEI, Q. HUA, P. H. MA and J. Q. BAO, *Inorg. Chem. Commun.* **5** (2002), 147.
11 D. YI, G. T. ZHANG, S. Y. ZHANGX. M. HUANG, W.C. YU and Y. T. QIAN, *Chem. Mater.* **12** (2000) 2845.
12 D. Q. DONG, J. WANG, J. Q. YYANG, J. ZHONG and Y. F. LIU, *Funct. Mater.* **30** (1999) 559.
13 Y. DING, H. Z. ZHAO, Y. G. SUN, G. T. ZHANG, H. WU and Y. T. QIAN, *Intern. J. of Inorg. Mater.*, **3** (2001) 151.
14 *OLI Systems Inc., OLI Software*, U.S.A. 2002.

Received 30 August 2004
and accepted 14 April 2005