J Mater Sci (2010) 45:177–181
DOI 10.1007/s10853-009-3913-x

Synthesis and formation of alumina whiskers from hydrothermal solution

**Jie Li · Wu Li · Xueying Nai · Shaoju Bian ·
Xin Liu · Ming Wei**

Received: 14 May 2009 / Accepted: 19 September 2009 / Published online: 6 October 2009

Abstract Al_2O_3 whiskers with an average length of 5 μm have been synthesized from hydrothermal solution. $Al(NO_3)_3$ and urea were mixed and put into a Teflon-lined stainless steel autoclave and then treated at 120 °C to fabricate precursor whiskers $NH_4Al(OH)_2CO_3$ (AACH). AACH whiskers were heated at 1200 °C in a furnace to obtain Al_2O_3 whiskers. The time-dependent examinations revealed that the formation process of AACH whiskers involves two sequential processes: a short liquid–solid deposition process in the initial stage and a long Ostwald ripening process. During calcinations, AACH transforms to amorphism then to α-Al_2O_3. The escape of NH_3 and CO_2 induced the distortion and toothlike morphology on the surface of the Al_2O_3 whiskers.

Introduction

The research of certain small, single crystal whiskers has attracted extensive interest especially for physicists and material scientists for many years due to their wide range of potential applications in industrial realm. Various kinds of whisker products, such as MgO [1], AlN [2], and $Al_{18}B_4O_{33}$ [3] have been reported and published in peer-reviewed publications during last decade. The high melting point, elastic modulus, thermal and chemical stability of alumina whiskers makes it one of the most important materials in the whiskers family.

It has been suggested that alumina whiskers are significant functional materials which can be widely used as reinforcement agents in the preparation of ceramic, metal, and polymer composite in order to improve their mechanical and high temperature properties [4, 5]. Many efforts have been put forward to obtain single crystal alumina whiskers. Webb and Forgeng [6] first fabricated alumina whiskers by heating alumina or $TiAl_3$ between 1300 and 1450 °C in the stream of hydrogen. This vapor deposition process was described by Devries and Sear [7], Edwards and Happel [8], Wiedemann and Sturzenegger [9], and Hayashi et al. [10]. Alumina whiskers were made using Al and SiO_2 powders via VLS deposition in Ar atmosphere at 1300 to 1500 °C [11–13]. Al and different metal oxide powders were used in Ar atmosphere at 850 to 1100 °C to obtain alumina whiskers [14, 15]. Okada et al. [16] synthesized alumina whiskers by decomposition of alumina borate whiskers. Yu and Du [17] prepared alumina whiskers by aluminum ethoxide precursor. Zhang [18] used titanium dioxide powder and aluminum powder as materials to form alumina whiskers. However, all these methods are expensive, time-consuming, required uncommon raw materials and often involve in tough reaction environment, such as high temperature processing, so the effortless and inexpensive manufacture process of alumina whiskers is in highly urgent demands.

In this article we proposed a new and economic process to fabricate alumina whiskers with very cheap and readily available raw materials at relatively low temperature. The growth process and mechanism of precursor whiskers and final products are discussed as well.

J. Li · W. Li (✉) · X. Nai · S. Bian · X. Liu · M. Wei
CAS Key Laboratory of Salt Lake Resources and Chemistry,
Qinghai Institute of Salt Lakes, Chinese Academy of Sciences,
Xining 810008, China
e-mail: driverlaoli@163.com

J. Li
Graduate University of Chinese Academy of Sciences,
Beijing 100049, China

Experimental

All of the chemical reagents used were of analytical grade and without further purification. Aluminum nitrate ($Al(NO_3)_3·9H_2O$) and urea were purchased from Tianjin Chemical Reagents Company. In a typical procedure, 7.5 g $Al(NO_3)_3·9H_2O$ and 3.6 g urea were mixed with 20 mL distilled water. After 30 min of stirring, the resulting solution was transferred into a Teflon-lined stainless autoclave (45 cm^3 capacity). The autoclave was sealed and maintained in an electric oven at 120 °C for 24 h, and then cooled to room temperature naturally. The product was carefully collected and washed with distilled water and then dried at room temperature. After that the precursor was calcined at 1200 °C for 4 h to get the final product.

X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). SEM images were taken on a JEOL JSM-5610LV SEM instrument. Thermogravimetric (TG) measurements were conducted on a TA SDT Q600 analyzer.

Results and discussion

Formation of precursor AACH whiskers

The liquid phase reactions of the system are shown below:

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2 \quad (1)$$

$$CO_2 + H_2O \rightarrow HCO_3^- + OH^- \quad (2)$$

$$NH_4^+ + Al^{3+} + HCO_3^- + 3OH^- \rightarrow NH_4Al(OH)_2CO_3 + H_2O \quad (3)$$

Hydrolyzation of urea produced plenty of NH_4^+, OH^-, and HCO_3^- in the solution [19]. These ions reacted with

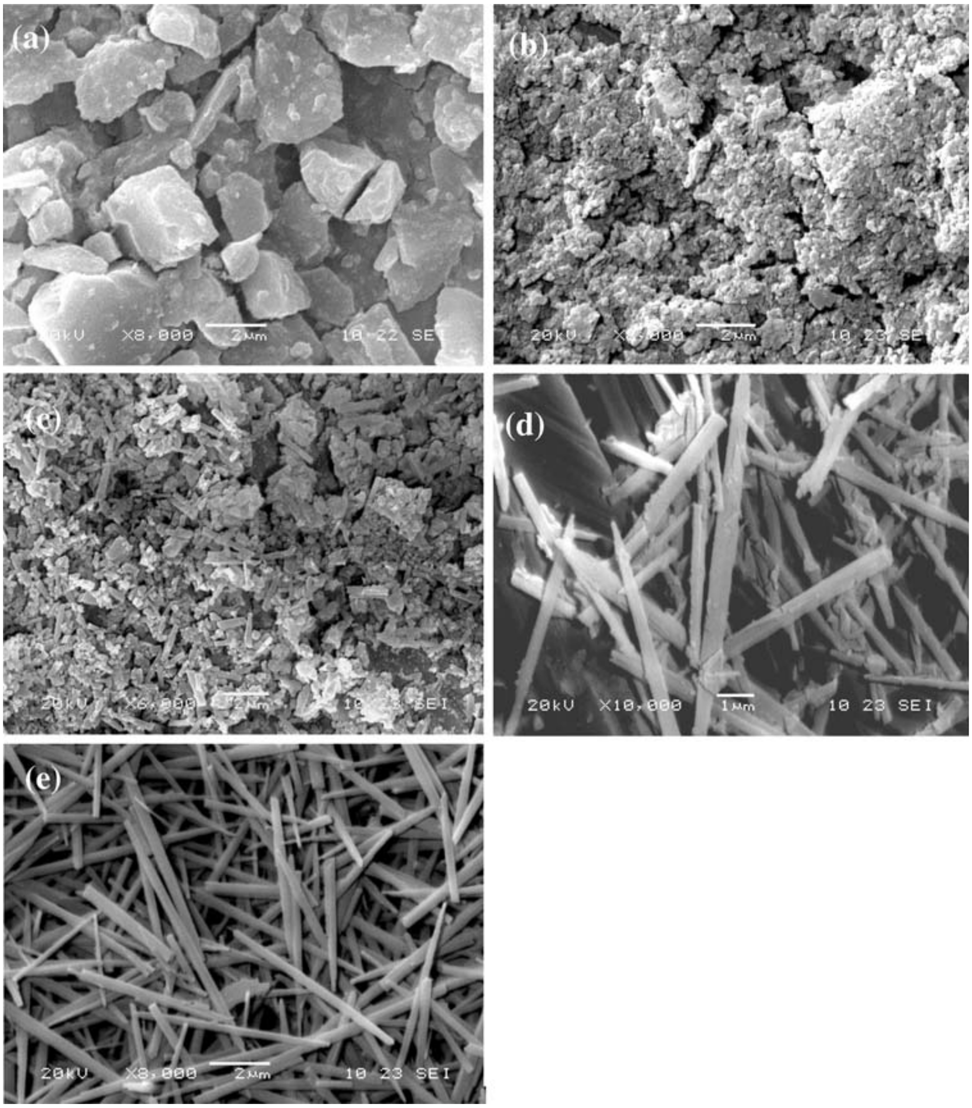

Fig. 1 SEM images of the AACH samples at different growth stages: **a** 1.5 h, **b** 3 h, **c** 4 h, **d** 5 h, **e** 8 h

Al^{3+} to form the precursor $NH_4Al(OH)_2CO_3$ (AACH). To understand the formation mechanism of AACH whiskers, we systematically investigated the samples obtained at different stages of the reaction using the SEM and XRD techniques. Figure 1a–e shows the SEM images of the samples obtained after the reaction proceeded for 1.5, 3, 4, 5, and 8 h, respectively. These images clearly demonstrate the transformation process of the particle morphologies from irregular particles to rodlike shape, and finally to whiskers structure. When the reaction proceeded for 1.5 h, the sample was composed mainly of irregular particles with different size and relatively smooth surface, as shown in Fig. 1a. These particles were viscid to some extent and were aggregated. The XRD pattern (Fig. 2a) of these particles shows no reflections, suggesting that they might be amorphous. When the reaction proceeded for 3 h, plenty of little hillocks emerged on the surface. The relatively smooth surface became rough (Fig. 1b). Two diffraction peaks appeared in the XRD pattern (Fig. 2b), suggesting that the crystallization process began. When the reaction proceeded for 4 h, these little hillocks extended to rods. The rodlike products had an average length of about 2 μm (Fig. 1c). The inorganic phase was indexed, AACH with good crystallinity was grown up (Fig. 2c). When the reaction proceeded for 5 h, plenty of whiskers were noticed in the sample, only a tiny percent of very small irregular particles could be observed in Fig. 1d. The length of these whiskers was 5–10 μm. When the reaction proceeded for 8 h, large scale of whiskers appeared. The length scale was the same as in Fig. 1d, but the rough surface changed to smooth and the irregular particles disappeared. The XRD patterns of last samples (Fig. 2d, e) show that well-crystallized AACH whiskers had formed. The series of SEM and XRD images reveals the transition process of the AACH whiskers.

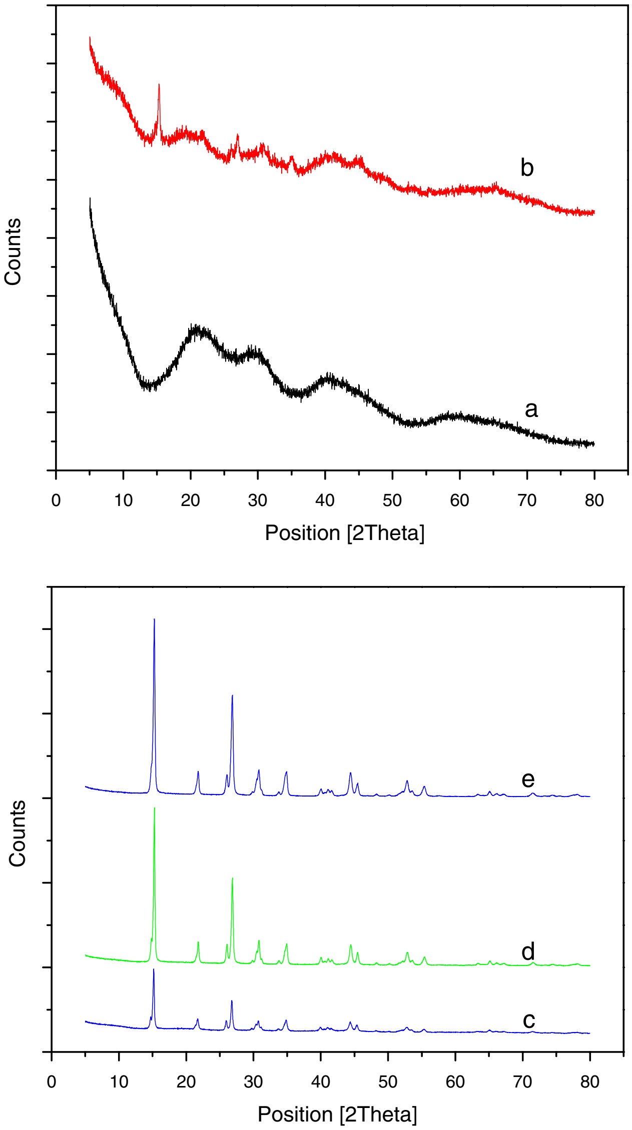

Fig. 2 XRD patterns of the AACH samples obtained at different growth stages: *a* 1.5 h, *b* 3 h, *c* 4 h, *d* 5 h, *e* 8 h

The above investigation suggests that the formation of AACH whiskers undergoes four distinctive stages: (1) the formation of irregular particles through the solvothermal reactions; (2) the growth of rodlike products from these irregular particles; (3) the formation of whiskers from the rodlike products; (4) the evolution of long and smooth whiskers. Such a formation process of AACH whiskers is depicted schematically in Fig. 3a–e. The stages involve a liquid–solid transformation process from $Al(NO_3)_3$ to AACH and a ripening process. The former process is performed in a relatively short period of the reaction time (5 h), and the latter process can last 3 h to 2 days to make sure the little irregular particles totally turn into whiskers.

The hydrothermal temperature is a key factor that influences the formation and particle size. The temperature affects the hydrolyzation of urea. No reaction occurs below 70 °C. The hydrolyzation rate increases with the raising temperature, but side reaction happens when the temperature is up to 130 °C, resulting in biuret and cyanuric acid formation. In our system, the efficient deposition started at 100 °C. At 90 °C, no matter how long the reaction lasts, only gel can be obtained. The morphology of the gel is the same as that of the product shown in Fig. 1a.

AACH whiskers has been synthesized as precursor, it can decompose to alumina products by calcining at certain temperature. We chose three temperature points to study the calcining stage in the range of 800–1500 K. XRD, TG, and SEM analysis were used to testify the products.

Formation of final alumina whiskers

AACH was sintered at 823, 1373, and 1473 K, respectively. The XRD patterns of the products obtained at different temperature is shown in Fig. 4. At 823 K,

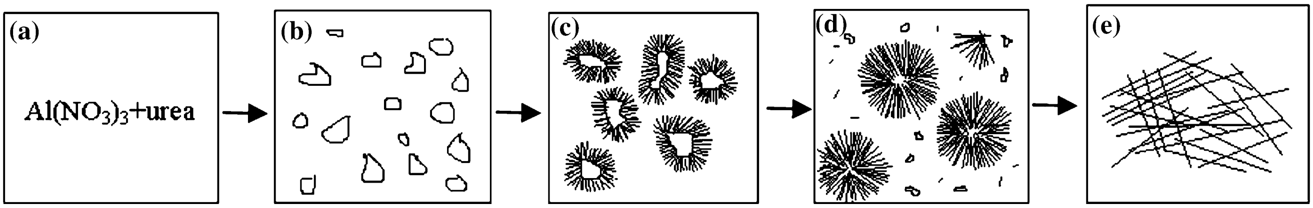

Fig. 3 Schematic illustration of the formation process of AACH whiskers: **a** initial solution; **b** 1.5 h, irregular particles; **c** 2 h, AACH whiskers appearing from the surface; **d** 4 h, AACH whiskers with few smaller irregular particles; **e** 5 h, long smooth AACH whiskers

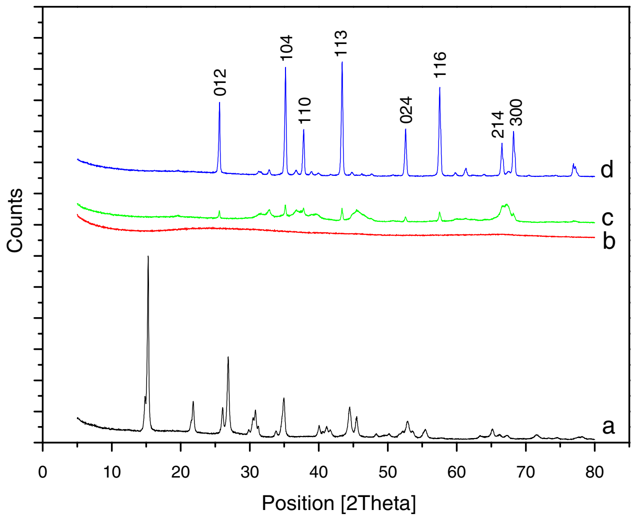

Fig. 4 XRD patterns of the alumina products obtained at different temperatures: *a* AACH, *b* 823 K, *c* 1373 K, *d* 1473 K

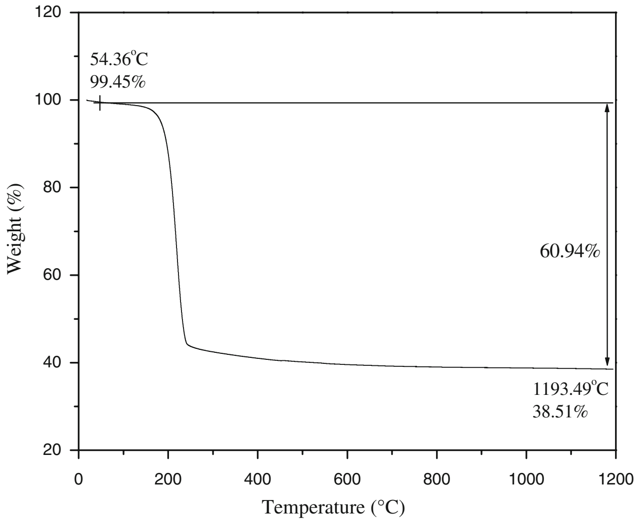

Fig. 5 TG curve of the precursor

amorphous products came forth (Fig. 4b). No diffraction peaks appeared on the XRD pattern. At 1373 K, the products were partly crystallized (Fig. 4c). The crystallization extent was better than the former. At 1473 K, distinct diffraction peaks show that α-Al_2O_3 with lattice constants $a = 4.758$ Å, $b = 4.758$ Å, and $c = 12.991$ Å were formed (Fig. 4d), in good agreement with the literature values (JCPDS Card No. 01-010-0173). In addition, the intense and sharp diffraction peaks suggested that the final products were well-crystallized.

The results testified that the AACH transformed to amorphous products initially and then to α-Al_2O_3. The TG curve (Fig. 5) shows that the precursor underwent a single-step weight loss (60.94%), which was very close to the net weight loss (ca. 63.3%) of pure AACH. These results indicated that AACH decomposed according to the following reaction:

$$2NH_4Al(OH)_2CO_3 \rightarrow Al_2O_3 + 2NH_3 + 2CO_2 + 2H_2O$$

The morphology and dimension of the products were examined by SEM. Comparison of the precursor and the final products are shown in Fig. 6a, b. The uniform AACH whiskers were around 10 μm long. The length of Al_2O_3 products was shorter than AACH whiskers, ranging from 1 to 5 μm. Besides, the smooth surface of AACH had turned to be distortion and toothlike. That was because the precursor AACH liberated NH_3 and CO_2 gas during conversion.

The structure of AACH crystal is composed of chains of Al–O octahedron [20] linked by sharing oxygen atoms with strong covalent bonds, CO_3^{2-} and NH_4^{+} are located between the chains associated by weak bonds, such as hydrogen bands [21]. During the decomposition of AACH, the Al–O chains kept constantly, NH_3, CO_2, and H_2O emitted and left gaps between the chains. When the gas molecules were liberated, the surface of whiskers was prone to be broken, especially when the gas volume evolved was large and the evolution quick.

Conclusions

In summary, alumina whiskers have been successfully synthesized. AACH whiskers were fabricated in the hydrothermal process and the alumina whiskers were obtained in the calcination process. The formation of the

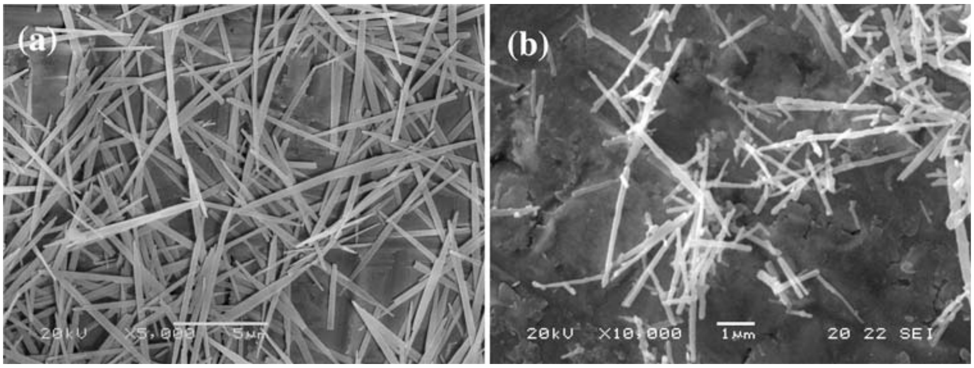

Fig. 6 Comparison of AACH and Al_2O_3 whiskers: **a** AACH whiskers: **b** Al_2O_3 whiskers

AACH whiskers went through the morphological changes from irregular particles to rodlike shapes and finally to whiskers structures, and these changes involved a short-period liquid–solid deposition process and a subsequent long-period ripening process. The formation of alumina whiskers underwent from amorphous state to crystalline state, escaping of NH_3 and CO_2 induced the distortion and the formation of toothlike structure. The synthesis process is proved to be efficacious for the preparation of alumina whiskers.

Acknowledgements The authors would like to thank the Western Personnel Training Plan of Chinese Academy of Sciences (No. 0810071031) and the Science and Technology Office of Qinghai province for financial support.

References

1. Shi QZ, Liu YC, Gao ZM, Zhao Q (2008) J Mater Sci 43:1438. doi:10.1007/s10853-007-2306-2
2. Wang HB, Northwood D (2006) J Mater Sci 41:1697. doi:10.1007/s10853-006-2939-6
3. Kim SW, Lee SG, Kim JK, Kwon JY, Park HC (2004) J Mater Sci 39:1445. doi:10.1023/B:JMSC.0000013914.91971.8b
4. Milewski JV (1992) Polym Compos 13:223
5. Parvizi-Majidi A (2005) Whiskers. Department of Mechanical Engineering and the Materials Science Program, Newark University of Delaware, United States, p 1
6. Webb WW, Forgeng WD (1957) J Appl Phys 28:1449
7. Devries RC, Sear GW (1959) J Chem Phys 31:1256
8. Edwards PL, Happel RJ (1962) J Appl Phys 33:826
9. Wiedemann HG, Sturzenegger E (1974) Naturwissenschaften 61:65
10. Hayashi T, Mihoya M, Yamai I, Saito H, Hirano SI (1987) J Mater Sci 22:1305. doi:10.1007/BF01233126
11. Valcarcel V, Souto A, Guitian F (1998) Adv Mater 10:138
12. Valcarcel V, Cerecedo C, Guitian F (2003) J Am Ceram Soc 86:1683
13. Cerecedo C, Valcarcel V, Gomez M, Guitian F (2006) J Am Ceram Soc 89:323
14. Li YF, Qin CD, Ng DHL (1999) J Mater Res 14:2997
15. Ng DHL, Yu P, Ma NG, Lo CK, Kwok WY, Yau MY, To CY, Li TK, Deng CJ (2006) J Eur Ceram Soc 26:1561
16. Okada K, Mutoh H, Otsuka N, Yano T (1991) J Mater Sci Lett 10:588
17. Yu ZQ, Du YW (1998) J Mater Res 13:3017
18. Zhang LZ, Zhang CC (2005) Key Eng Mater 280–283:1021
19. Janeković A, Matijević E (1985) J Colloid Interface Sci 103:436
20. Mitsui I (1977) Nippon densi zairyo Gijutsu Kyokai Shu-ki Keon Gaiyoshu 14:5
21. Ma CC, Zhou XX, Xu X, Zhu T (2001) Mater Chem Phys 72:374