Preparation and growth mechanism of AlN whiskers by combustion synthesis with Y_2O_3 as additive

WENKUI LI*
Jiangxi Key Laboratory of Surface Engineering, JiangXi Science and Technology Normal University, P. R. China; Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China
E-mail: liwenkui1976@163.com

BAOLIN ZHANG, HANRUI ZHUANG, WENLAN LI
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

Published online: 3 February 2006

Aluminum nitride has been widely acknowledged as one of the most promising materials for use as an electrical substrate and package material because of its high thermal conductivity, excellent electrical insulation, and thermal expansion coefficient close to that of silicon. Whiskers were used extensively to reinforce and toughen ceramic and glass matrix composites. The earliest report about the growth of AlN whiskers is thta of Kohn's experiment. Following that, AlN whiskers have been extensively studied [1, 2].

Combustion synthesis (CS) has emerged as an important technique for the synthesis and processing of advanced ceramics, catalysts, composites, alloys, intermetallics, and nanomaterials [3–7]. Combustion synthesizing AlN whiskers have been studied, and the effects of amide additives, experimental conditions, and impurity content on the final composition and morphology were investigated. The AlN whisker growth mechanism was discussed and the vapor–solid (VS) growth mechanism model was established [5, 8–11]. However, there are few reports about the effect of oxide additives on the combustion synthesis of AlN whiskers. Now, oxide additives, especially rare-earth oxides, have been used to promote the growth of whiskers, in conventional and unconventional methods, by forming a liquid phase. As a result of this, this paper introduces Y_2O_3 as an additive during combustion synthesis of AlN whiskers, and the growth mechanism is discussed.

Commercially available reactant powders Al (5.0 μm), Y_2O_3 (0.52 μm), and AlN (0.50 μm) were used to synthesize AlN whiskers. The raw materials were mixed for 24 hr, according to the weight ratio list in Table I, using absolute ethanol as the milling media. The powder mixture was dried and then passed through a 40-mesh sieve. The combustion synthesis experiments were performed in a cold isostatic pressure vessel under 5 MPa nitrogen pressure. The samples were placed in a porous graphite crucible and the reaction was initiated by the igniting titanium powder placed on top of the mixtures. In order to make clear the growth mechanism of AlN whiskers, a quenching device was used, which is shown in Fig. 1.

Phase analysis of the combustion products was performed by using X-ray diffractometry (XRD). The morphologies of combustion products were studied by using scanning electron microscopy (SEM).

XRD analysis results (as shown in Fig. 2) indicate that most of the Al powder has been nitrided into AlN under the high nitrogen pressure. It is easily understood that Y_2O_3 reacts with AlN and the ever-present Al_2O_3 layer, which lies on the surface of Al and AlN particles, and forms a Y–Al–O–N grain-boundary phase existing in the form of a liquid under such a high temperature, because the combustion synthesis temperature is much higher than the melt point of the Y–Al–O–N system.

Fig. 3 shows the SEM micrograph of the combustion products with and without Y_2O_3 additive. The combustion product with Y_2O_3 additive shows a whisker morphology, while the combustion product without Y_2O_3 is mainly composed of short-column crystals.

It is difficult to perform *in situ* observation, because the combustion synthesis of AlN is a strong exothermic reaction in high temperature and under high pressure. Therefore, most of the evidence is obtained by the SEM from the morphologies of the combustion products. Fig. 4 shows the morphology of the different areas of the quenched sample.

In the present work, the AlN whiskers are mainly from the following reactions:

$$\mathrm{Al(s) \rightarrow Al(l); \quad Al(s) \rightarrow Al(g); \quad Al(l) \rightarrow Al(g);}$$

$$\mathrm{2Al(l) + N_2(g) \rightarrow 2AlN;}$$

$$\mathrm{2Al(g) + N_2(g) \rightarrow 2AlN;}$$

* Author to whom all correspondence should be addressed.

0022-2461
DOI: 10.1007/s10853-006-5334-4

TABLE I Initial composition of samples

Sample no	Composition of samples (wt %)		
	Al	AlN	Y_2O_3
A	50	50	0
B	47.6	47.6	4.8

It is known that the VS and VLS (vapor–liquid–solid) are the two main mechanisms for the formation of whiskers [12]. During the combustion synthesis of AlN whiskers in the quenching device, the copper crucible absorbed the heat generated by the exothermic reaction rapidly. Because of the absence of enough heat for grain growth, AlN whiskers stopped growing, as reflected by the morphologies of the partially grown AlN whiskers in Fig. 4. The cone tips, shown in Fig. 4, strongly suggest that the whiskers grow by the VLS mechanism. In the VLS mechanism, the reactant molecules from the vapor are deposited by diffusion through the VL interface to the LS (liquid–solid) interface. Precipitation occurs in the cone tip at the LS interface and the cone tips are lifted up from the substrate. The Y–Al–O–N cone tip liquid with its high accommodation coefficient provides an intermediate stage of crystallization at the VS interface. However, there are some platelets of AlN in the final morphology of sample B (as shown in Fig. 3B), which is characteristic of the VS mechanism. Therefore, both VS and VLS are not completely independent in the combustion synthesizing AlN whiskers using Y_2O_3 as additive. In our previous work, the reaction of Al and N_2 in the combustion synthesis is mainly by the VS mechanism, the addition of Y_2O_3 promote the role of the VLS mechanism by forming Y–Al–O–N liquid phase. This conclusion is consistent with the results of Wang's work on the effect of oxygen impurity on the morphology of AlN synthesized by combustion synthesis [5]: for a high oxygen impurity content, the VLS mechanism plays a more important role than the VS mechanism.

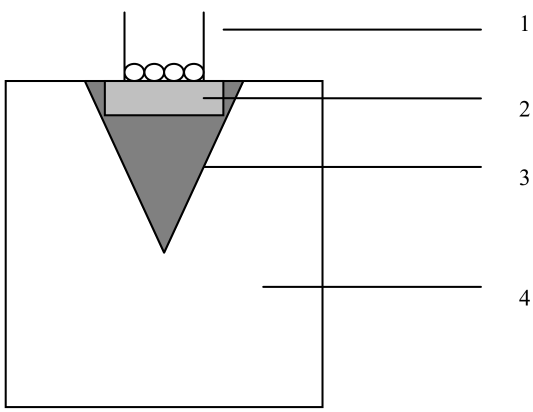

Figure 1 Schematic diagram of quenching assemble by copper crucible: (1) igniting tungsten wires, (2) the igniter of Ti powder, (3) the mixture of reactant, and (4) copper crucible.

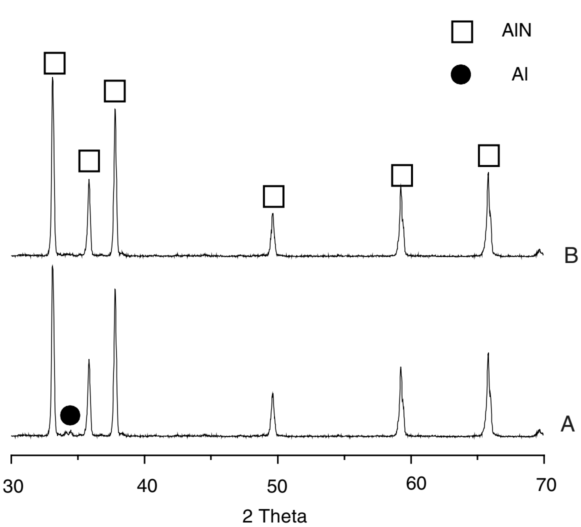

Figure 2 X-ray diffraction (XRD) pattern of combustion products: (A) without Y_2O_3, and (B) with 4.8 wt % Y_2O_3.

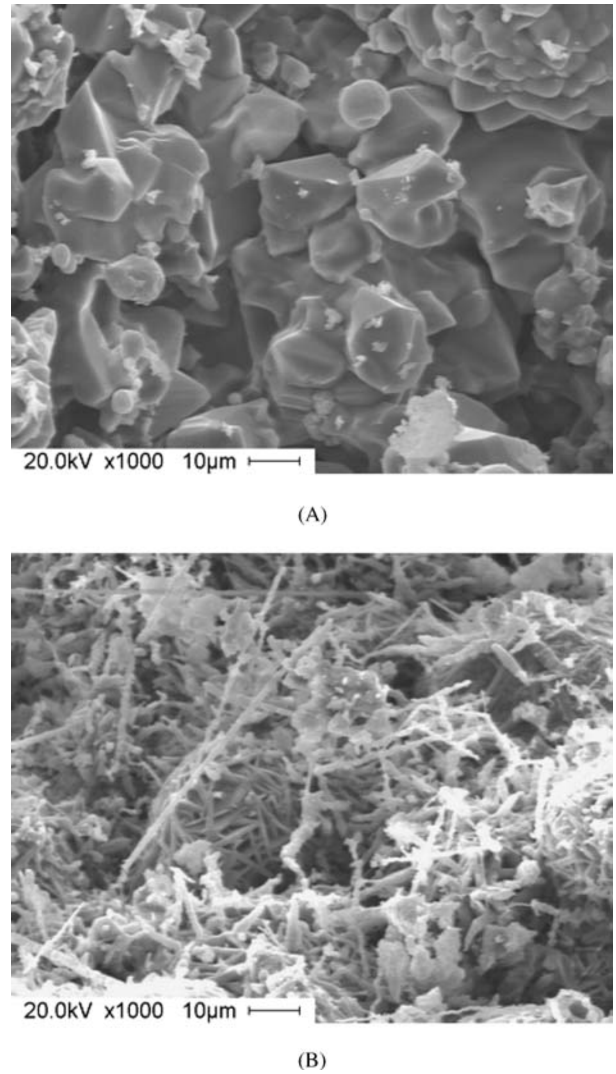

Figure 3 Typical morphology of combustion products: (A) without Y_2O_3, and (B) with 4.8 wt% Yl_2O_3.

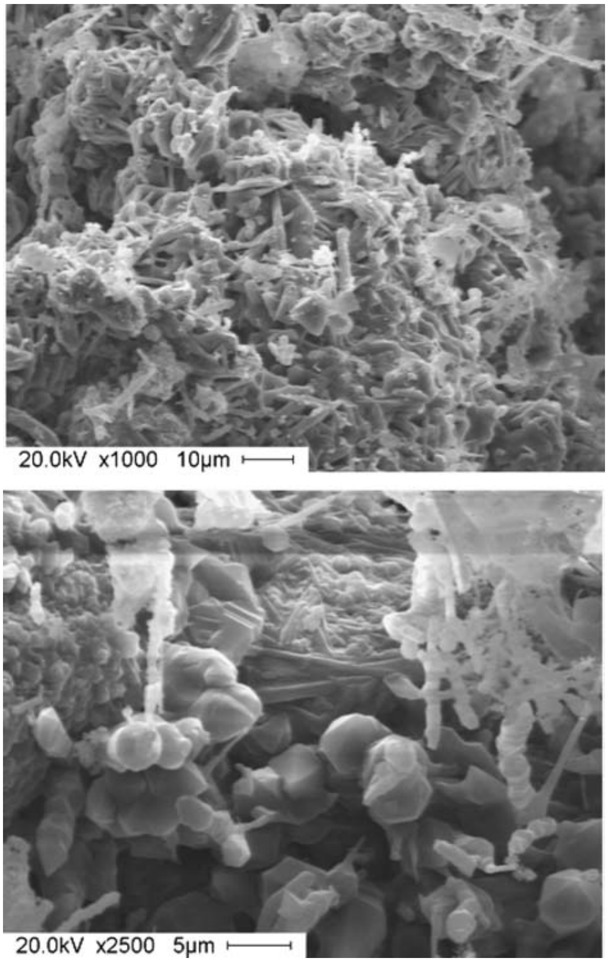

Figure 4 The morphology of quenched sample in different areas.

Considering the growth morphology of the AlN whiskers in the quenched sample and the final sample, the whole growth process includes the following stages: (1) with the initial heat generated by the Ti powders, the exposed Al surface reacted with N_2 and generated more heat; (2) the Y–Al–O–N liquid phase, formed due to the addition of Y_2O_3, removed the Al_2O_3 layer present on the surface of the Al powder and formed a new Al surface exposed to the N_2. This contributed to the melt and evaporation of the Al powder and promoted the nitridation and growth of the AlN whiskers; (3) the Y–Al–O–N liquid phase also provided an interface for the growth of AlN whiskers on those substrates of irregular geometry. The surface of the liquid had a large accommodation coefficient and was the preferred site for deposition of the "AlN vapor" (formed by Al and N_2). The liquid became supersaturated and the AlN precipitated from the supersaturated liquid at the solid–liquid surface. Eventually, the AlN whiskers grew by diffusion through the VL interface to the LS interface. The AlN, used as a diluent, also dissolved and deposited on the whisker surface. In some areas, the liquid phase was not sufficient, therefore, platelets of AlN formed by the VS mechanism; (4) a little Y–Al–O–N liquid phase has evaporated during the combustion process, while most of the liquid phase remained in the final products by forming glass phase during the cooling process. Therefore, no Y_2O_3 or any other crystalline phase except AlN was detected in the final products.

On the basis of the above discussion, a conclusion can be drawn that the addition of Y_2O_3 changed the AlN whisker growth mechanism during combustion synthesis, by forming Y–Al–O–N liquid phase. The addition of Y_2O_3 promoted the growth of AlN whiskers. The final morphology resulted from the synergy of VLS and VS mechanism.

References

1. Y. BAIK and R. A. L. DREW, *Key. Eng. Mater.* **122–124** (1996) 553.
2. J. A. KOHN, P. G. COTTER and R. A. POTTER, *Amer. Mineral.* **41** (1956) 355.
3. K. C. PATIL, S. T. ARUNA and S. EKAMBARAM, *Curr. Opin. Solid. State Mater. Sci.* **2** (1997) 158.
4. K. C. PATIL, S. T. ARUNA and T. MIMANI, *ibid.* **6** (2002) 507.
5. H. WANG, J. HAN, Z. LI and S. DU, *J. Europ. Ceram. Soc.* **21** (2001) 2193.
6. K. C. PATIL and S. T. ARUNA, in "Redox Methods in SHS Practice in Self-Propagating High Temperature Synthesis Materials," edited by A. A. Borisov, L. T. De Luca, A. G. Merzhanov and Y. N. Scheck (Taylor & Francis, New York, 2002).
7. A. G. MERZHANOV, "SHS Research and Development Handbook" (Chernogolovka, Russia: Russian Academy of Sciences, 1999).
8. R. FU, H. ZHOU, L. CHEN and Y. WU, *Mater. Sci. Eng. A* **266** (1999) 44.
9. J. BERMUDO and M. I. OSENDI, *Ceram. Int.* **25** (1999) 607.
10. J. GUOJIAN, Z. HANRUI, W. BENMIN, Z. JIONG and R. MEILING, *J. Syn. Cry.* **4** (1999) 382.
11. *Idem.*, *ibid.* **4** (1999) 387.
12. A. P. LEVITT, "Whisker Technology" (Wiley, New York, 1970).

Received 20 November 2003
and accepted 24 March 2005