Combustion synthesis of AlN whiskers

HUABIN WANG, DEREK O. NORTHWOOD*
Department of Mechanical, Automotive and Materials Engineering, University of Windsor, N9B 3P4, Canada
E-mail: dnorthwo@uwindsor.ca

JIECAI HAN, SHANYI DU
Center for Composite Materials, Harbin Institute of Technology, Harbin 150001, People’s Republic of China

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Long and coarse AlN whiskers comprising more than 80 vol% of the combustion product have been successfully produced through combustion synthesis. Addition of ammonia halides can accelerate the vaporization of Al, and retard the deposition rate of AlN, with the result that the growth of AlN whiskers is markedly promoted. A growth model for a spiral whisker by a helical screw dislocation mechanism, or a combination mechanism of a helical screw dislocation and the VLS process, is proposed. Periodic interactions of vacancies and the tip of a screw dislocation cause the growth of a spiral whisker in the model. Under an atmosphere of supersaturated “AlN vapor,” the growth of whiskers along the axial direction slows down and gradually arrests, due to the limitation of the diffusion distance. A series of deposition sites are then produced at regular, isolated locations along the center line on the prismatic plane, and eventually cause the formation of dendritic whiskers.

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1. Introduction
Aluminum nitride (AlN) ceramics have attracted much attention as a promising electrical substrate and packaging material, because of such properties as high thermal conductivity, excellent electrical insulation, low dielectric constant, and a thermal expansion coefficient closely matching that of silicon. AlN can also be used as an advanced refractory material, because of its non-wettability by molten aluminum and most of the nonferrous alloys. One example of the refractory use of AlN is as crucibles for the growth of single-crystal gallium arsenide. Another potential and very large market for AlN is as fillers to improve the thermal conductivity of epoxy [1, 2].

Powders comprised of larger particles, with a bimodal size distribution, are desirable for filler applications. Larger particles are less sensitive to high humidity, and a bimodal distribution results in higher packing density [3]. Whiskers are of interest for their small size, low defect content, and excellent mechanical and physical properties that are nearly equal to the theoretical values. AlN whiskers are preferred to powders for use as fillers. When polymers are reinforced with acicular AlN whiskers, their conductivity increases by a factor of 70 over that of the matrix [4]. Because heat flow occurs along conductive fillers, long and coarse whisker-type AlN is expected to significantly improve thermal conductivity.

Many fabrication methods for AlN whiskers had been developed, such as, the CVD method [4], vaporization and condensation of AlN powder [5–7], the direct nitridation of metallic aluminum [8] and the carbo-thermal reduction method [9–13].

Recently, self-propagating high-temperature synthesis (SHS), also known as combustion synthesis, of AlN whiskers has attracted considerable attention because it offers an energy- and time-saving process, as well as cost reductions. Bradshaw and Spicer found that different morphologies of AlN were associated with different sample regions and that AlN whiskers were especially predominant in the combustion product when 5 wt% of NH3 is added to the atmosphere [14]. Lee et al. obtained high-aspect-ratio whiskers under low nitrogen pressure by adding 3 wt% MgCl2 [15], and the volume ratio of whiskers to altolike structures increased gradually as the distance from the sample surface increased. However, Shin et al. [16] found that AlN whiskers generally occurred in the outer-layer of the sample, a finding that...
agrees with the results of our earlier research, where the morphology of the product was strongly related to its oxygen content [17]. Several types of whisker structure, such as wavy structure, crossed structure, stack structure, bead-necklace structure, branch structure, dendritic crystal, have been found in the combustion product due to variations in the growth conditions [18, 19].

Shin et al. attributed the formation of AlN whiskers to the condensation of an AlN vapor phase formed during SHS under fairly low nitrogen pressure (<1 MPa) [16]. Because no whiskers showed characteristic VLS (vapor-liquid-solid) droplets on their tips, Bradshaw and Spicer concluded that AlN whiskers grow via the vapor-solid (VS) mechanism, although they did not exclude the VLS mechanism [14]. However, the intermediate morphologies of both AlN particles grown by the VS mechanism and AlN whiskers grown by the VLS mechanism have been observed in gas-release experiments [17]. In our opinion, AlN particles develop from the vapor by the way of platelet growth (VS mechanism) at low oxygen contents. The growth of AlN whiskers is mainly controlled by the VLS mechanism [17].

The morphology, chemistry, and crystallography of the SHS of AlN were investigated by scanning electron microscopy (SEM) and X-ray diffractometry (XRD) in the present study. The effects of additives on the growth of whiskers, the growth mechanism of the spiral whisker, and the coarsening mechanism of AlN whiskers, are discussed in this paper.

2. Experimental procedures

Commercially available aluminum powders (Northeast Light-Alloy Co., Harbin, China), with an average particle size of ~22 µm were used as the reactant. AlN powders, fabricated by ourselves using combustion synthesis, were used as the diluant. NH₄Cl, NH₄F, were used as the additives.

The compositions of the starting mixtures are listed in Table I. After the mixtures of Al and AlN powders were first vacuum-dried, ammonia halides were added into them. They were ball-milled using twice alumina balls in a plastic container for 12 h. 1 kg of the mixtures was pressed into cylindrical compacts (10 cm in diameter and about 14 cm in length). The compact was placed in a graphite crucible. Some fine Ti powder as an igniter was put on the top of the compact. The crucible with the compact was put into a stainless steel combustion chamber. The air in the chamber was removed by purging twice with 0.5 MPa N₂. The chamber was then back-filled with commercial grade nitrogen at a pressure of 10 MPa. The compact was ignited by using a tungsten coil.

The phase composition and interplanar distances of the product were investigated by X-ray diffraction (XRD) using a Phillips X-ray diffractometer with a proportional counter detection head. Graphite monochromated Cu Kα radiation at a voltage of 40 KV and a current of 20 mA, was used. The morphology of the product was examined by a JEOL scanning electron microscopy (SEM). The operation voltage was 20 KV.

3. Results and discussion

The combustion product in sample A1 (without additives) is a porous, sintered body. The AlN particles are mostly coarse and regular as shown in Fig. 1a. AlN whiskers can occasionally be observed. The combustion products in the sample A2 (containing 5 wt% NH₄Cl) were not densely packed. They mainly consisted of AlN particles and some fine AlN whiskers between the particles (Fig. 1b). This indicates that the formation of AlN whiskers can be promoted by adding NH₄Cl.

Addition of NH₄Cl has two effects on the growth of AlN whiskers. First, the growth of AlN whiskers is mainly controlled by a VLS mechanism. The formation of liquid required in the VLS mechanism depends on the presence of impurities, especially impurities containing oxygen. The addition of NH₄Cl significantly increases the oxygen content in the combustion product [17]. Thus, addition of NH₄Cl can promote the growth of AlN whiskers. Second, NH₄Cl sublimes at 350°C and decomposes into ammonia and HCl vapor at 520°C. HCl vapor is driven to the combustion front by the high temperature of the combustion zone and reacts with aluminum at the combustion front. The reactions between HCl vapor and aluminum are as follows:

\[
2\text{Al}(s, l, g) + 2\text{HCl}(g) \rightarrow 2\text{AlCl}_2(g) + \text{H}_2(g) \quad (1)
\]

\[
\text{Al}(s, l, g) + 2\text{HCl}(g) \rightarrow \text{AlCl}_2(g) + \text{H}_2(g) \quad (2)
\]

\[
2\text{Al}(s, l, g) + 6\text{HCl}(g) \rightarrow 2\text{AlCl}_3(g) + 3\text{H}_2(g) \quad (3)
\]

where \(s, l, g\) in brackets denote solid, liquid and gas states, respectively. Because of the surplus of Al and a deficiency of HCl vapor, Reaction (1) is the most favorable. Besides the above reactions, there is a vaporization reaction of Al.

\[
\text{Al}(s, l) \rightarrow \text{Al}(g) \quad (4)
\]

With respect to the amount of vaporized Al, Reaction (4) is the dominant mechanism. However, from the viewpoint of thermodynamics, Reaction (1) is more favorable than Reaction (4).

Subsequently, Al and AlCl vapor react with nitrogen and generates “AlN vapor” in the approaching combustion zone.

\[
\text{Al}(g) + \text{N}_2(g) \rightarrow \text{AlN}(g) \quad (5)
\]

\[
2\text{Al}(g) + 2\text{NH}_3(g) \rightarrow 2\text{AlN}(g) + 3\text{H}_2(g) \quad (6)
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al (wt%)</th>
<th>AlN (wt%)</th>
<th>NH₄Cl (wt%)</th>
<th>NH₄F (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>50</td>
<td>50</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>A2</td>
<td>50</td>
<td>45</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>A3</td>
<td>50</td>
<td>42</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

TABLE I Composition of the initial mixtures in samples A1, A2, and A3