

Effect of additives on self-propagating high-temperature synthesis of AlN

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Abstract

Effect of additives on the oxygen content and the growth mechanism of self-propagating high-temperature synthesis (SHS) of AlN were investigated in detail. Although the addition of NH₄Cl made the product loosen, it also increased the water vapor concentration of the system at the same time, which brought a great increase of the oxygen content in the product. Carbon decreased the oxygen content of AlN by two kinds of mechanisms: carbothermal reduction of Al₂O₃, and decrease of the water vapor concentration that served as the catalyst of AlN oxidation at elevated temperature. The latter was found to be the dominant mechanism. Partly carbonized sucrose decreased the oxygen content of AlN more significantly than black carbon due to its ever-increasing surface area, arising from its carbonization during combustion. At the lower oxygen content, AlN grew from the vapor in the form of “platelet growth”. With increasing oxygen content, the growing steps were blocked up by the impurities containing oxygen. The “platelet growth” was gradually inhibited, and AlN inclined to grow into whiskers by VLS mechanism. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Aluminum nitride (AlN) ceramics has attracted much attention as an ideal electrical substrate and package material because of its high thermal conductivity, excellent electrical insulation, and thermal expansion coefficient close to that of silicon. If incorporated into polymer as a filler, AlN would also improve the thermal conductivity of plastic package materials as made. AlN can yet be found many applications as advanced refractory materials for it is not dissolved or eroded by molten Al and most of the non-ferrous alloys. It is predicated that the market of AlN ceramics at the end of year 2000 will have cost approximately 550 million dollars just in the electronics field.¹

In general, submicrometer AlN powders (about 3 m²/g surface area) with rather low content of residual metals (< 35 ppm Fe), oxygen (< 1.2 wt.%) and carbon (< 0.1 wt.%) are ideal for electronics substrate and packaging applications. However, the powders, comprised of larger

particles and a bimodal size distribution, are most desired in filler applications.²

Theoretically predicated to be 320 W/mK,³ the intrinsic thermal conductivity of AlN would be severely degraded by even a small concentration of dissolved impurity, especially for oxygen because an oxygen atom dissolved into the crystalline lattice of AlN and generating a vacancy at an aluminum site at the same time, works as a phonon severely scattering site.^{4–12} Whereas AlN, that has strong affinity of oxygen, easily takes place hydrolysis and oxidation. It is a challenge to obtain AlN powder with a low oxygen content.

AlN powders are produced commercially either via direct nitridation of aluminum powders in a nitrogen atmosphere at high temperature or via carbothermal reduction of alumina with carbon. A rapid, direct nitridation process had been developed from direct nitridation by Weimer et al.² In addition, AlN can be synthesized by chemical vapour deposition (CVD), polymer pyrolysis, and arc plasma methods

Self-propagating high-temperature synthesis offers an energy and time-saving process for preparing AlN powder as well as low contamination, high conversion, and cost reduction, etc. Research on SHS of ceramic powders

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was initiated from the pioneering works of Merzhanov et al., in the late 1970s. Bradshaw et al.¹³ found that different morphologies of AlN were associated with different region and AlN whiskers predominated in the combustion product, especially when 5% of NH₃ had been added into atmosphere. But they cannot determine the growth mechanism of AlN whiskers since no tip droplet was found on the tip of whiskers.¹⁵ Shin et al.,¹⁴ discussed formation mechanism of AlN during SHS under fairly lower nitrogen pressure (< 1 MPa). Whereas, it is not very clear under what condition AlN developed into whiskers and particles during combustion.

The oxygen content of self-propagating high-temperature synthesized AlN without any additives was rather low (1 < wt.%). The oxygen content rapidly went up to 9.15 wt.% from 0.4 wt.% after being ball-milled in alcohol for 24 h.¹⁷ Some impurities were also introduced into the powders. Thus, some halide salts, such as NH₄Cl, etc., were required to add into the reactants as a loosening agent. In addition, a certain amount of AlN was also needed in order to prevent molten Al drops from aggregation and improve conversion ratio.

The effect of additives on the oxygen content and the growth mechanism of AlN were also studied in details in this paper. In order to make clear the growth mechanism of AlN, a new technology (gas-releasing method) was developed.

2. Experiment procedure

Commercially available Al powders (Northeast Light-alloy Co.) with an average particle size of about 22 μm, and self-made AlN powders by SHS with an average particle size about 2.7 μm were used as reactant and dilute in this study, respectively. Their chemical compositions are summarized in Table 1. NH₄Cl and two kinds of carbon source (carbon black, and sucrose, the latter was partly carbonized at 200° C under vacuum for 6 h) were added as additives into the reactants.

The starting mixtures of the composition, listed in the Table 2, were prepared by vacuum-drying, and then ball-milled twice with Al₂O₃ balls in a plastic container for 24 h. The loose mixture of approximately 80 g was put into a crucible. Oxygen gas in the chamber was removed by means of pumping into and then out at 5 atm N₂ twice. Then the chamber was back-filled with 100 atm nitrogen.

Table 1
Chemical composition of initial powders

Element	Al	N	O	Si	Fe	C	Others
Al	>99.5	–	0.24	0.12	0.04	0.02	Trace
AlN	<0.2 ^a	31.4	3.70	–	0.06	–	Trace

^a Free Al content in AlN powder.

Table 2
Composition of the initial mixture in samples

Sample	Al (wt.%)	AlN (wt.%)	NH ₄ Cl (wt.%)	Carbon black (wt.%)	Sucrose (wt.%)
A1, A6 ^a	50	50	–	–	–
A2, A7 ^a	50	45	5	–	–
A3	50	44	5	1	–
A4	50	43	5	2	–
A5	50	43.2	5	–	1.8 ^b

^a A6 and A7 are used in gas-releasing experiment.

^b Approximately 1.8 g partly carbonized sucrose is equivalent to 1 g carbon.

The self-propagating reaction was initiated by igniting the pre-piled fine Ti powders on the top of the mixture with a heating tungsten coil.

Combustion temperature was measured with a W-5%Re vs W-26%Re thermocouple, connected with a data-collecting system. The junction of the thermocouple was placed in a hole of the sample, 20 mm from the top. Morphology of the product was examined with scanning electron microscopy (SEM). The contents of oxygen and carbon in the product were investigated with RO-316 and CS-344 (LECO Co., USA), respectively. The elemental compositions in some micro-areas are analyzed using X-ray energy dispersive spectroscopy (EDS).

In order to make clear the growth mechanism of AlN, a gas-releasing technology was developed. Most of the procedure of the gas-releasing experiments was similar with SHS experiments besides that, nitrogen gas was very rapidly released from the chamber in the gas-releasing experiments while combustion wave was proceeding along the sample. Because released nitrogen gas carried a large amount of heat away, afterburning was inhibited and combustion was quenched. We can induce what happened in SHS reaction on basis of the information that was protected from afterburning

3. Results and discussion

3.1. The oxygen content of AlN

The oxygen and carbon content of samples with different amount of additives are summarized in the Table 3. The oxygen content in the sample A1(without

Table 3
Oxygen and carbon content of product in samples with different additives

Content	Initial	A1	A2	A3	A4	A5
O (wt.%)	3.70	3.10	5.90	5.05	4.64	2.64
C (wt.%)	–	–	–	0.69	1.47	0.63

any additives) was about 3.10 wt.% lower than 3.70 wt.% of the initial dilutes. Because combustion temperature of SHS reaction was up to 2000° C the combustion product in the sample A1 is very hard to be crushed into powders. This is due to self-sintering. The oxygen content rapidly went up during crushing.¹⁵ The samples containing NH₄Cl were fairly loose. However, the addition of NH₄Cl brought a great increase of oxygen content. The oxygen content in the sample A2, A3, A4 and A5 were approximately 5.90, 5.05, 4.64 and 2.64 wt.%, respectively. It is notable that consumption of carbon in samples A3 and A4 is not in proportion with the decrease of the oxygen content. Partly carbonized sucrose decreased the oxygen content of AlN more significantly than black carbon.

Generally, NH₄Cl at the front of combustion wave had decomposed into ammonia and HCl vapor. Both ammonia and HCl vapor would react with “Al vapor” during combustion, and generate hydrogen gas, which might react with the oxygen gas from nitrogen, and form water vapor. In addition, adsorbed water in the NH₄Cl, resulted from its previous treatments, also turned into water vapor at the front of combustion wave. The water vapor is thought to be a catalyst of the oxidation of AlN at elevated temperature,¹⁷ which may be the reason of a great increase of the oxygen content with addition of NH₄Cl.

Carbon can decrease the oxygen content of AlN by two mechanisms: the carbothermal reduction of Al₂O₃, and decreasing of the water vapor concentration. The carbothermal reaction, a solid-solid reaction, was limited by the contact area between Al₂O₃ and C, which was generally very small due to the limited amount of carbon. From the result that consumption of carbon was not in proportion with the decrease of the oxygen content, it can be deduced that the carbothermal reaction was not the main means of decreasing the oxygen content. The reaction between carbon and water vapor was determined by the surface area of carbon. Further carbonization of the sucrose during combustion created a much larger surface area than common black carbon. Thus, it can significantly decrease the water vapor concentration. A little amount of carbon consumption can greatly decrease the oxygen content of AlN by inhibiting the catalytic reaction of AlN oxidation.

3.2. Morphology of AlN

Morphology of SHS of AlN particles in the sample A1 (without any additives) were regular and coarse equiaxed crystal as shown in Fig. 1a. AlN whiskers were hardly visible in the product. However, sample A2, A3 and A4 (containing 5 wt.% NH₄Cl) consisted of fine AlN whiskers as shown in Fig. 1b, c and d, which agreed with Bradshaw's results. Although AlN whiskers can be occasionally spotted, sample A5 mostly consisted of fine equiaxed AlN crystal as shown in Fig. 1e. In

addition, the amount of AlN whiskers in the out-layer of all samples was higher than that in the center. According to our results, the oxygen content of AlN in the out-layer of the samples was generally higher than that in the center. It is obvious that the morphology of the product was closely related to its oxygen content. The higher the oxygen content of AlN, the higher the volume of AlN whiskers.

3.3. The growth mechanism of AlN

In the gas-releasing experiments, nitrogen gas was very rapidly released from the chamber while combustion wave proceeded along the sample. Because the release of nitrogen gas carried a larger amount of heat away, combustion was quenched. The intermediate growing morphology of AlN was protected from the afterburning.

Morphology of AlN particles in sample A6 was irregular (close to sphere), and many steps can be viewed on the surface of AlN particles in the shape of a pyramid as shown in Fig. 2a. The nucleus and small steps on the top of the pyramid were right hexagonal, and the larger steps at the bottom of the pyramid were circle-shaped. The configuration of surface steps illustrated that AlN must grow in the form of “platelet growth” from the vapor (vapor-crystal growth mechanism, VC). The height of the steps that were seen in Fig. 2a significantly outweighs the height of individual atomic steps. In fact, every step should be a step cluster consisting of many close-knit small steps with an atomic height, described as platelet growth by Elbaum and Chahalmers.

According to their theory, a uniform distribution of steps may be unstable against local fluctuation in density and velocity, leading to a configuration in which the steps are bunched together. Consider an impurity that is adsorbed on the surface, but is present in a small amount so that it takes a relatively long time to reach equilibrium. The impurity is supposed to impede the movement of a step. If the step temporarily lags a little behind its proper position the surface ahead of it will absorb more impurity, so that its motion will become more and more slow. The step ahead of it will continue to move at the same speed, or may even accelerate as it has less competition from the diffusion field of the slow-moving step, so that it will move further away. The steps behind the slow-moving one will continually close upon it to smaller than normal distances, since they are meeting a clean surface, and will only slow down to the limiting velocity of the slow step when the diffusion field effect forces them to do so.¹⁶ Above all the result is that the aggregates of individual steps separated from each other by large distances are visible under a microscope as large surface steps.

According to the Volmer–Becker theory, anisotropy surface energy is the controlling factor in determining

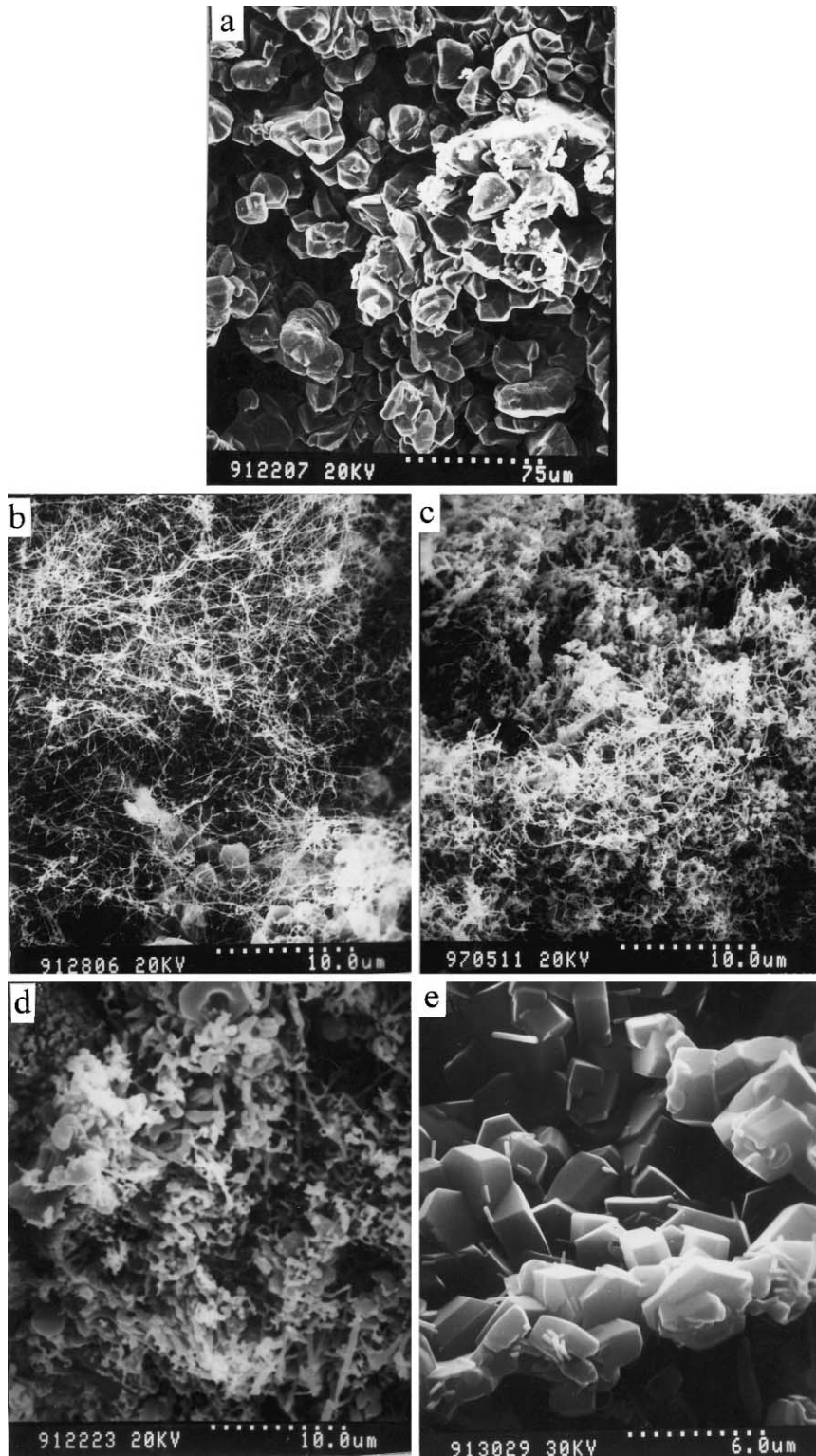


Fig. 1. Morphology of SHS of AlN in the samples: (a) A1, (b) A2, (c), A3, (d), A4, (e) A5.

the shape of the stable nucleus.¹⁶ Because the surface energy of the {0001} and {1010} plane of AlN are the lowest and the second lowest, respectively, the hexagonal two-dimensional nucleus on the close-packed crystallographic plane is the most stable one. Therefore,

the nucleus and the following small growing steps must keep themselves regular hexagonal due to their surface energy. At the same time, the hexagonal steps suggested that the deposited plane of AlN vapor is a {0001} close-packed crystallographic plane. The difference of the

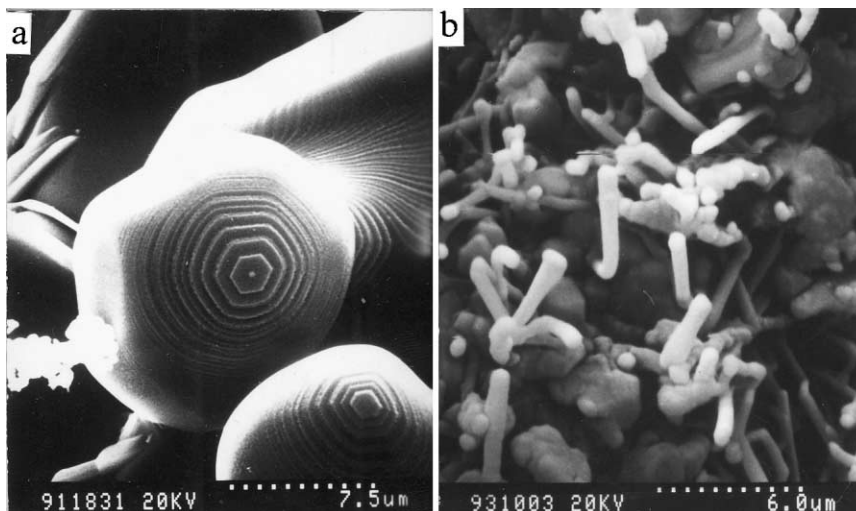


Fig. 2. Morphology of the growing AlN in the gas-released samples: (a) A6, (b) A7.

surface energy for a different face becomes small, and for macroscopic crystals the surface energy is negligible in comparison with the volume energy. The shape of a macroscopic crystal is governed, in practice, by the rates of growth of the various faces. An atom preferentially attaches itself at the center of a step rather than at the end of a step. Hence, the larger steps are close circle due to their higher rate of growth at the center.

However, the nucleus and small steps would be re-vaporized and deposited on the larger steps at the stage of afterburning because of their higher surface energy. Hence the surface of AlN particles in the sample A1 was flat, and no step was found on their surface. Because released nitrogen gas carried a larger amount of heat away in the gas-releasing experiments, afterburning was inhibited. In other words, the nucleus and small steps had no time to be re-vaporized and deposit on the larger steps. Therefore, these steps were protected from after-burning.

Morphology of AlN in the sample A7 was very interesting as shown in Fig. 2b. Many “liquidlike” globules were observed on the surface of irregular particles. The globules were often found at the tip of the whisker. The elemental analysis by EDS showed that these globules contained oxygen as shown in Fig. 3, which greatly suggested that AlN whiskers grew by the vapor–liquid–solid (VLS) mechanism.^[17,18]

Why can the addition of NH_4Cl promote AlN to grow in the form of whiskers? The reasonable interpretation might be given as follows: at lower oxygen content, AlN grew in the form of “platelet growth” from the vapor (VC mechanism). However, while NH_4Cl , as a loosening agent, was added into the reactants, the oxygen content of AlN rapidly increased to 5.90 wt.%. With respect to the new synthesized AlN, its oxygen content reached 7.51 wt.%. If oxygen existed in the form of Al_2O_3 , the Al_2O_3 content in the new synthesized AlN would be

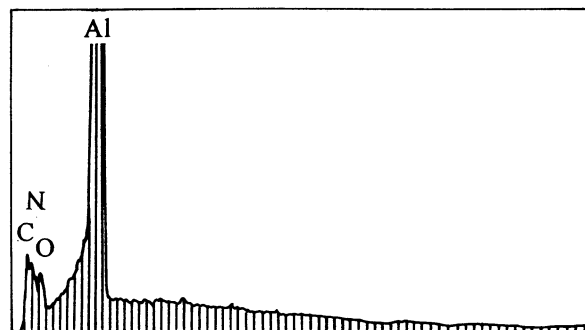


Fig. 3. EDS pattern of the globule at the tip of AlN whisker.

approximately 16 wt.%. If oxygen existed in the form of AlON, it would take up to 26 wt.% in the new synthesized AlN. The molecules containing oxygen impurity, such as AlON molecules, were preferentially adsorbed at the fast growing steps in order to reduce surface energy. The deposition of the impurity molecules on the steps can prevent them from growing. As the oxygen content was so high in the samples with NH_4Cl , and, therefore, most of the steps were blocked up, it was very difficult for AlN to continually grow in the form of “platelet growth”.

At the same time, there were many tiny liquid globules in some oxygen-rich micro-area on the surface of AlN. It was expected that combustion temperature of all samples (above 2400°C) was higher than the melting point of Al_2O_3 (2045°C). The surface of the liquid had a large accommodation coefficient and was a preferred site for deposition of “AlN vapor”. The liquid became supersaturated with the vapor deposition happening. AlN precipitated from the supersaturated liquid at the solid–liquid surface. Eventually, AlN whiskers grew by

diffusion through the vapor–liquid (VL) interface to the liquid–solid (LS) interface. The laminate AlN particle that the arrow shows at the top right corner of Fig. 2b, was a typical one. The particle firstly grew in the form of the platelet growth. As the growing steps were blocked up, some small liquid globules began to appear in some oxygen-rich micro-area on the surface of AlN before the sample was quenched. Because the oxygen content of AlN was decreased by the addition of the partly carbonized sucrose, AlN grew in the platelet growth mechanism again.

4. Conclusion

1. The addition of NH_4Cl made the product loosen, but it also increased the water vapor concentration of the system at the same time, which produced a great increase of the oxygen content of AlN.
2. Carbon decreased the oxygen content of AlN by means of two kinds of mechanisms: carbothermal reduction of Al_2O_3 and decrease of the water vapor concentration, a catalyst of oxidation of AlN at elevated temperature. The latter is the dominant mechanism. The partly carbonized sucrose had a more significant effect on the oxygen content of AlN than black carbon. This is due to the fact that once the sucrose was further carbonized during combustion, it would get a much larger surface area.
3. At the lowest oxygen content, AlN grew in the form of “platelet growth” from the vapor (VC mechanism). With an increase of the oxygen content, AlN gradually tended to grow in the form of a whisker by VLS mechanism.

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