

# Combustion synthesis of aluminum nitride powder using additives

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Aluminum nitride powder was synthesized by a combustion synthesis method using various additives. Each additive was mixed with Al powder, and the powder mixture was then pressed into a compact. The combustion reaction was ignited by heating the compact under N<sub>2</sub> atmosphere of 0.4 MPa. Additives containing halogens were found to have a catalytic effect on the combustion reaction. High product yields were obtained when using additives of NH<sub>4</sub>X, CO(NH<sub>2</sub>)<sub>2</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOH, and CO<sub>2</sub>H(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H. In all these cases, eggshell-like skins were observed to form on the Al particles at the early stage of combustion. The catalytic effect, formation of the eggshell-like skins, and their effects on the combustion process were investigated and discussed.

## I. INTRODUCTION

Aluminum nitride is among the most exciting technical ceramics currently under development for high-tech applications. Commercial interests result from the remarkable combination of its properties such as high thermal conductivity, high electrical resistivity, good corrosion and thermal-shock resistance, low thermal expansion coefficient, and a low dielectric constant.<sup>1,2</sup> It has been considered for many applications, such as electronic substrates, packaging materials for integrated circuits, heat sinks, high thermally conductive composite materials, and hardware for containing or processing molten metals and salts.<sup>3,4</sup> Although many processes have been developed for manufacturing AlN powders,<sup>5</sup> development of new processes for producing AlN powder at low cost is still an interesting research topic.

Our research objective has been to investigate the use of combustion synthesis (SHS) method for the production of AlN powder. The SHS method, originally developed in the former USSR,<sup>6</sup> has been applied to synthesis of various materials including ceramics, intermetallics, and composites. It has many potential advantages such as low processing cost, energy-efficiency, and high production rate.<sup>7</sup>

In the combustion synthesis of AlN from Al and N<sub>2</sub>, since the combustion temperature is much higher than the melting point of Al, Al particles will melt before

proceeding with combustion. To synthesize AlN under low nitrogen pressures, it is essential that the Al particles do not coalesce during heating and combustion. If this occurs, the nitrogen available to the combustion reaction will be limited to inside the pores because coalescence of the Al particles inhibits N<sub>2</sub> from diffusing into the compact. As a result, a high N<sub>2</sub> pressure will be required to complete the combustion reaction and to achieve a high product yield.

In our previous study,<sup>8</sup> a SHS method was developed for the synthesis of AlN powder under low nitrogen pressures. In this method, NH<sub>4</sub>X (X = F, Cl, Br, or I) was added to Al and the powder mixture was pressed into a compact, which was placed in a reaction chamber filled with N<sub>2</sub>. The combustion reaction was ignited by heating the compact, and high product yields were obtained under nitrogen pressures of around 0.5 MPa. The compact was observed to retain its shape and to become highly porous during heating. Nitrogen thus could diffuse easily into the compact, resulting in complete combustion and high product yields. Since a compact composed of only Al particles (i.e., no additives) could melt and collapse during heating, NH<sub>4</sub>X was considered to be capable of preventing the Al particles from coalescence. However, the details and the mechanism of this effect remained unclear.

In this work, four different types of compounds (i.e., additives including NH<sub>4</sub>X) were examined for their capability of preventing the Al particles from coalescence. The details and the mechanism of this effect were investigated. Also investigated were their effects on the combustion process and the product yield.

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## II. EXPERIMENTAL

Listed in Table I are the characteristics of the reagents used in the present study. The additives are classified in four groups: (i) those containing both  $\text{NH}_x$  and X (halogens); (ii) those containing only  $\text{NH}_x$  ( $\text{NaN}_3$  is considered to contain  $\text{NH}_x$ , where  $x = 0$ ); (iii) those containing only X; (iv) those containing neither  $\text{NH}_x$  nor X. Aluminum powder and one of the additives were thoroughly mixed at the desired proportions, and 1 g of the mixture was pressed into a cylindrical compact (referred to as reactant compact or compact) by applying a pressure of approximately 169 MPa. (The compact compositions are all expressed as weight ratios in the present study.) The compact thus formed had a diameter of 10 mm and a length of approximately 8 mm. The reaction chamber used in the present study has been shown schematically in our previous study.<sup>9</sup> The reactant compact was placed on a height-adjustable stage, which was adapted so that the top surface of the compact was 2–3 mm below the heating element, a graphite plate (instead of a tungsten coil). The reactor was evacuated to 650 Pa by flushing with nitrogen between the evacuations. After the evacuations, the reactor was back-filled with nitrogen at the desired pressure (0.1–0.5 MPa). The combustion reaction was ignited by heating the top surface of the reactant compact with an electric current (approximately 600 W) passing through the graphite plate. The heating power was turned off after ignition. (Note that by using

a graphite plate as heating element, the electric power required for ignition was greatly reduced as compared to 1600 W in our previous study<sup>8</sup> where a tungsten coil was used.)

Variation of the temperature at the top surface of the reactant compact was measured by using 0.127-mm-diameter W 3% Re–W 25% Re thermocouples. As shown in Fig. 1, the thermocouple insulated with 1.2-mm-diameter alumina tube was held to form an angle of approximately  $30^\circ$  with the top surface of the compact. The thermocouple junction was placed at the center of the top surface where a shallow hole (0.5-mm diameter and 0.2-mm deep) had been drilled. The thermocouple was pressed down with a small pressure to assure a good contact with the top surface.

Formation of the product was determined by x-ray diffraction (XRD) analysis. The quantity of residual Al in the product was determined by a gas evolution technique.<sup>10</sup> Approximately 100 ml of 15 wt% HCl was added to 5 g of the combustion product which had been ground to  $d_{50} \sim 5 \mu\text{m}$ . The quantity of the residual Al was obtained by calculation from the volume of the hydrogen gas thus evolved. The product yield was defined as the weight ratio of the Al that had been converted to AlN to that initially contained in the reactant compact. The morphology of the product was analyzed with a scanning electron microscope (SEM), and elementary analysis was carried out with an energy dispersive x-ray

TABLE I. Characteristics of the reagents.

Category	Reagent	Particle size	Purity (%)	Mp (K)
Reactant	Al	-325 mesh	99.5	943
	$\text{N}_2$		99.9	
Additive	(i) Containing both $\text{NH}_x$ and X			
	$\text{NH}_4\text{F}$		92	468 <sup>a</sup>
	$\text{NH}_4\text{Cl}$		99	610 <sup>a</sup>
	$\text{NH}_4\text{Br}$		99	664 <sup>a</sup>
	$\text{NH}_4\text{I}$		GR grade	620 <sup>a</sup>
	(ii) Containing only $\text{NH}_x$			
	$(\text{NH}_4)_2\text{CO}_3$		99	330 <sup>a</sup>
	$\text{NH}_4\text{HCO}_3$		99	333 <sup>a</sup>
	$\text{CO}(\text{NH}_2)_2$		99	406
	$\text{NaN}_3$		99	603 <sup>a</sup>
	(iii) Containing only X			
	$\text{AlCl}_3$		99	450 <sup>b</sup>
	$\text{NaCl}$		99	1164
	$\text{KI}$		97	954
	(iv) Containing neither $\text{NH}_x$ nor X			
	$\text{KNO}_3$		99	606 (673 <sup>a</sup> )
$\text{Ba}(\text{NO}_3)_2$		99	865	
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$		99	343	
$\text{CO}_2\text{H}(\text{CH}_2)_2\text{CO}_2\text{H}$		99.8	458	

<sup>a</sup>Decomposition.

<sup>b</sup>Sublimation.

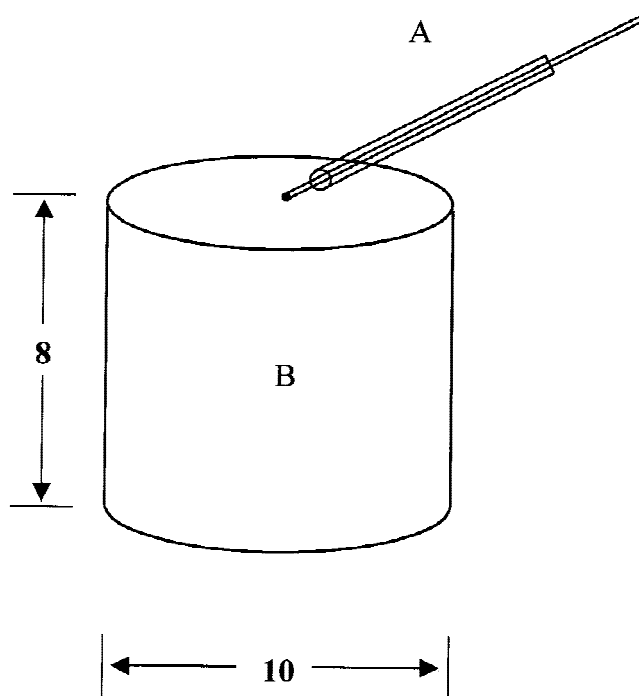


FIG. 1. Configuration and location of the thermocouple for temperature measurements: (A) thermocouple; (B) reactant compact (unit: mm).

spectrometer (EDS). The particle size distribution was measured by a centrifugal-sedimentation particle size analyzer.

### III. RESULTS

#### A. Combustion phenomena and temperature variations

Depending on the type of additive used, two different kinds of combustion phenomena were observed. When using additives which melt upon heating [e.g.,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , and  $\text{CO}_2\text{H}(\text{CH}_2)_2\text{CO}_2\text{H}$ ], a liquid film appeared on the outside surface of the upper portion of the reactant compact as the heating power was turned on. The liquid film was seen vaporizing as evidenced by bubbling and smoke evolution. Appearance of the liquid film and its bubbling and smoke evolution was observed to propagate down the compact, which was similar to the propagation of a combustion wave. After disappearance of the bubbling liquid film and completion of the smoke evolution, another liquid film was observed to form at the top surface of the compact and, subsequently, ignition of the compact was observed to occur (indicated by a glow of red light). When using these additives, typical temperature–time histories measured at the top surfaces of the reactant compacts are shown in Fig. 2 where urea and stearic acid were taken as examples. Also shown in Fig. 2 was the temperature–time

history of a reactant compact without any additives for purpose of comparison. In each case, the temperature was seen to increase as the heating power was turned on. After a thermal equilibrium was reached approximately 1773 K, the temperature increases abruptly. This abrupt increase in temperature was coincident with the visual ignition of the combustion reaction. The temperature at the point of the abrupt increase was thus defined as the ignition temperature. The thermocouple was soon burned out after ignition due to a substantial increase in temperature. In the case of using urea or stearic acid as additive, the combustion wave propagated down the compact very quickly and reached the bottom end of the compact within 1 s. In the case of no additives, the combustion reaction extinguished soon after ignition, leaving a large portion of the compact unreacted. Each profile in Fig. 2 is also seen to have a drop in temperature at its early stage of heating. When using urea or stearic acid as additive, the temperature drop was coincident in time with visual appearance of the liquid film; it was thus considered to be caused by melting of the additive. When using a compact without any additives, the temperature drop was considered to be caused by melting of Al particles. It is noted that this temperature drop occurred at a temperature higher than that when using urea or stearic acid, following the order of their melting points (see Table I).

When using additives which decompose or sublime upon heating (e.g.,  $\text{NH}_4\text{X}$  and  $\text{AlCl}_3$ ), evolution of smoke from the top surface of the reactant compact was observed as the heating power was turned on. This evolution of smoke propagated down the compact, appearing similar to the propagation of a combustion wave, which has been described in our previous study.<sup>8</sup> Ignition was observed to occur at the top surface of the compact during propagation of the smoke evolution. Shown in Fig. 3 are typical temperature–time histories measured at the top surfaces of the reactant compacts. Temperature drops were also measured during heating and were observed to be coincident in time with the onset of smoke evolution. These temperature drops were thus considered to be caused by decomposition or sublimation of the additives. The time periods of heating required for ignition to occur (defined as ignition times) were much shorter than those shown in Fig. 2. The ignition times and ignition temperatures for various additives are listed in Table II. Since the increase in temperature due to ignition in cases such as these two was not apparent (compared to those shown in Fig. 2), their ignition times were determined by visual observation. Propagation of combustion in these two cases was much slower than those shown in Fig. 2. Furthermore, the combustion was observed to occur twice as evidenced by twice of visible glow of red light, which is also in agreement with the two peaks in the temperature profiles.

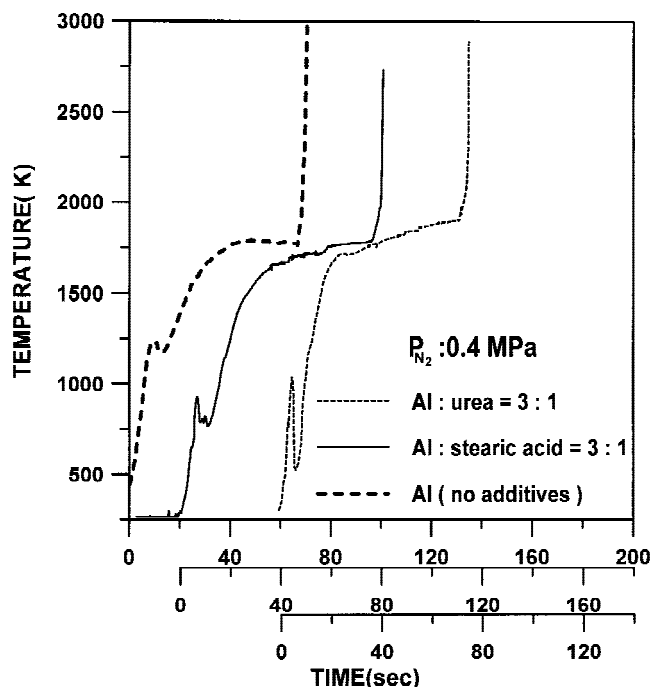


FIG. 2. Typical temperature–time histories of reactant compacts containing urea, stearic acid, and no additives.

## B. Effect of additives on product formation

Figure 4 shows the XRD patterns of the products synthesized using additives containing both  $\text{NH}_x$  and X (i.e., ammonium halides). As can be seen, the relative intensity ratios of the characteristic peaks of AlN to Al follow the order of the measured product yields for these additives. Among these, the product yield when using  $\text{NH}_4\text{F}$  was the highest where no residual Al was detected. However,  $\text{AlF}_3$  was detected to form in the product. Figure 5 shows the XRD patterns of the products synthesized using additives containing only  $\text{NH}_x$ . Among the four  $\text{NH}_x$ -containing compounds, urea  $[\text{CO}(\text{NH}_2)_2]$  generates the

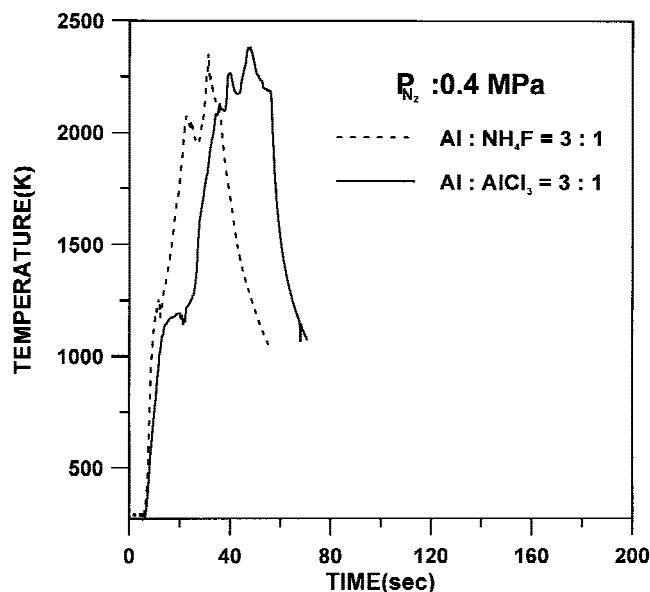


FIG. 3. Typical temperature–time histories of reactant compacts containing  $\text{NH}_4\text{F}$  and  $\text{AlCl}_3$ .

TABLE II. Ignition times and ignition temperatures for various additives.

Additive	Ignition time (s)	Ignition temp. (K)
$\text{NH}_4\text{F}$	30–40	1300–1500
$\text{NH}_4\text{Cl}$	30–40	1300–1500
$\text{NH}_4\text{Br}$	30–40	1300–1500
$\text{NH}_4\text{I}$	30–40	1300–1500
$\text{AlCl}_3$	20–30	1300–1500
$\text{CO}(\text{NH}_2)_2$	80–100	Approximately 1850
No additives	80–100	Approximately 1850
$\text{NH}_4\text{HCO}_3$	80–100	Approximately 1850
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	80–100	Approximately 1850
$\text{CO}_2\text{H}(\text{CH}_2)_2\text{CO}_2\text{H}$	80–100	Approximately 1850
$\text{NaN}_3$	N <sup>a</sup>	
$\text{NaCl}$	N	
$\text{KI}$	N	
$\text{KNO}_3$	N	
$\text{Ba}(\text{NO}_3)_2$	N	

<sup>a</sup>N: could not be ignited.

highest product yield. The compact containing  $\text{NaN}_3$  could not be ignited; instead it melted and collapsed during heating. Figure 6 shows the XRD patterns of the products synthesized using additives containing only halogens. When using  $\text{AlCl}_3$  as additive, the product yield was lower than those when using ammonium halides (see Fig. 4), and the product contained a small amount of oxide, which might be caused by the moisture adsorbed on  $\text{AlCl}_3$ . When using either  $\text{NaCl}$  or  $\text{KI}$  as additive, combustion reaction could not be ignited and the compact was observed to melt and collapse during heating. Figure 7 shows the XRD patterns of the products synthesized using additives containing neither  $\text{NH}_x$  nor X. As can be seen, the product yields when using stearic acid and succinic acid are much higher than that using  $\text{KNO}_3$  or  $\text{Ba}(\text{NO}_3)_2$ , where, in addition to large amounts of residual Al, oxides were also detected.

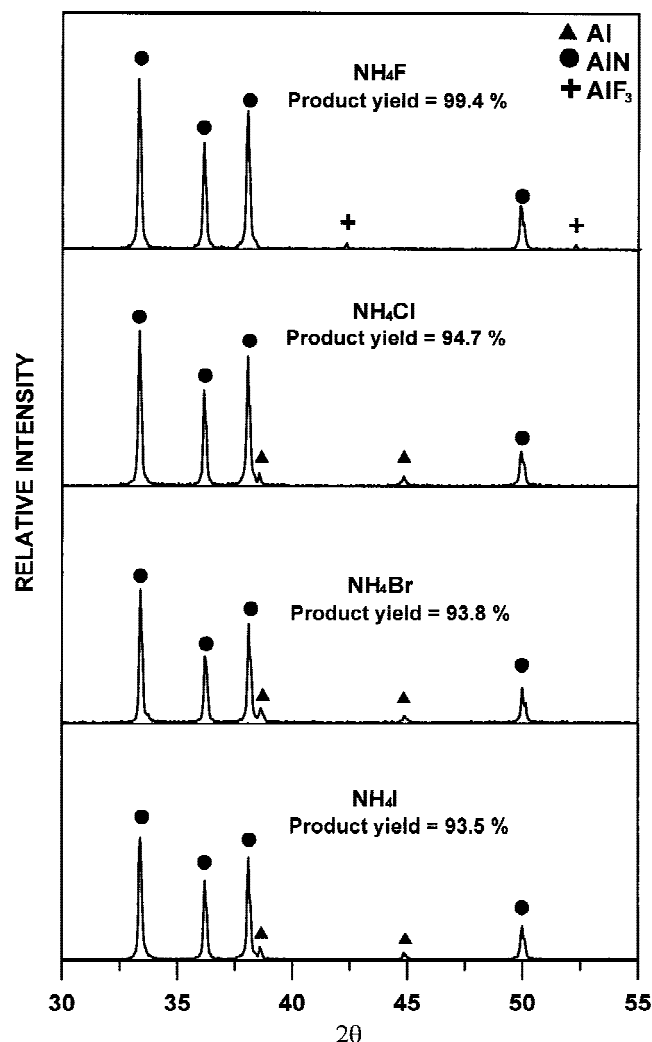


FIG. 4. XRD patterns of the products synthesized using additives containing both  $\text{NH}_x$  and X (Al:additive = 3:1; nitrogen pressure = 0.4 MPa).

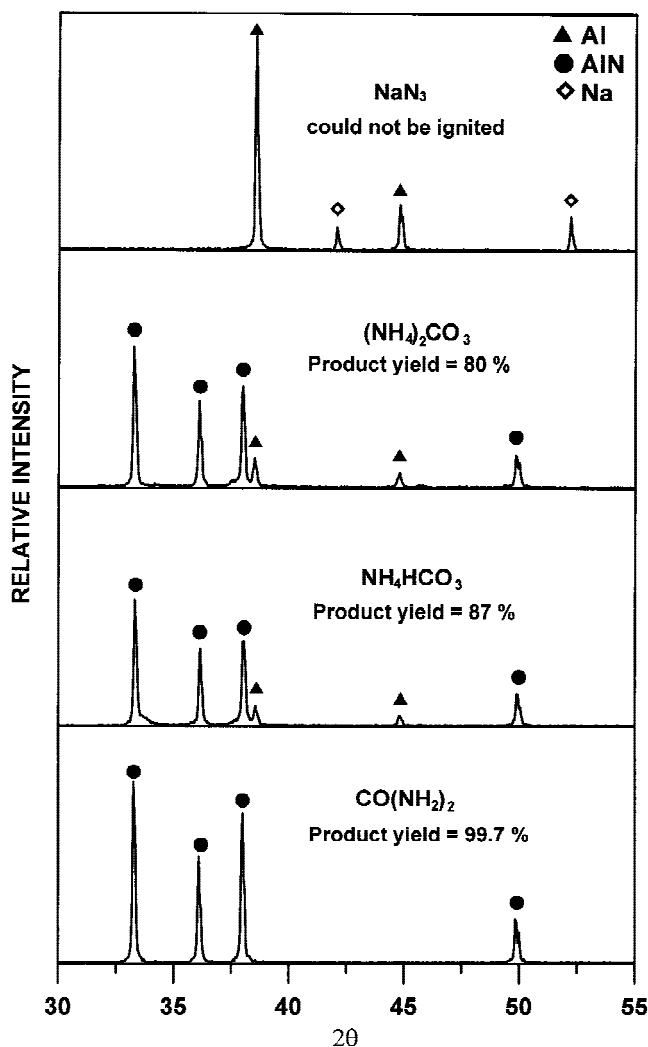


FIG. 5. XRD patterns of the products synthesized using additives containing only  $\text{NH}_x$  (Al:additive = 3:1; nitrogen pressure = 0.4 MPa).

### C. Effect of additives on reaction process

To investigate the effects of additives, several reactant compacts containing different additives were heated under Ar atmosphere for approximately 100 s. The compact melted and collapsed when it contained no additives or contained  $\text{AlCl}_3$ . However, the compact retained its shape and became highly porous when it contained  $\text{NH}_4\text{X}$ , urea, stearic acid, or succinic acid. These porous compacts could be ignited and brought into complete combustion after replacing the Ar with  $\text{N}_2$  in the reaction chamber. Figure 8 shows the XRD patterns of the compacts after being heated under Ar atmosphere. As can be seen, a small amount of AlN was detected for the compact initially containing  $\text{NH}_4\text{F}$  but no AlN could be detected for other compacts. The compacts containing urea, stearic acid, and succinic acid became gray to dark in color after heating, which might be caused by deposition of carbon from decomposition of the additives.

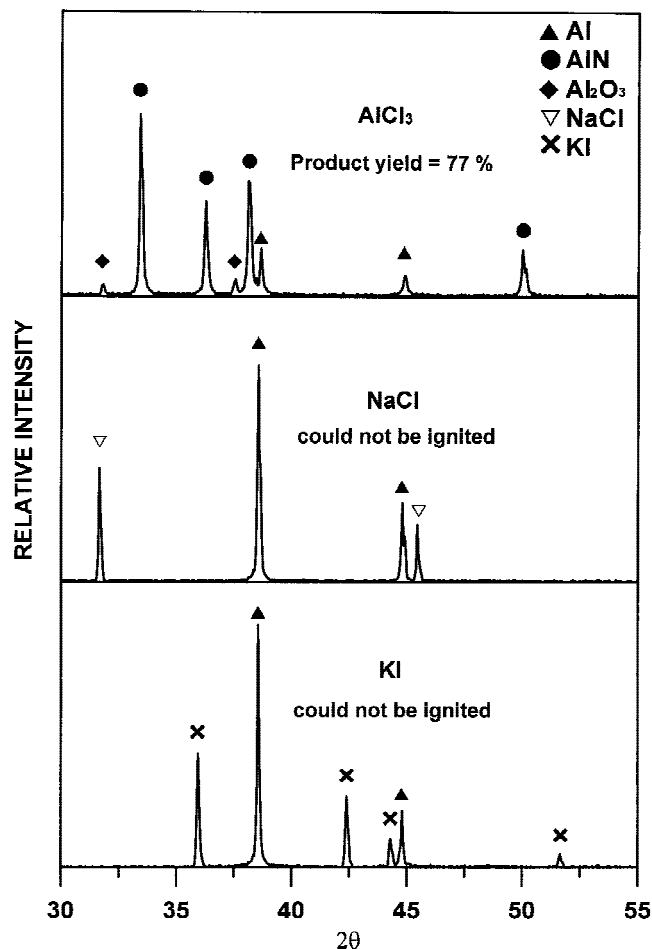


FIG. 6. XRD patterns of the products synthesized using additives containing only X (Al:additive = 3:1; nitrogen pressure = 0.4 MPa).

Figure 9 shows typical SEM photographs of the fractured surfaces of the compacts which had been heated for approximately 100 s under Ar atmosphere. Listed in Table III are the elementary compositions of various spots shown by arrows on the SEM photographs. In the case of using  $\text{AlCl}_3$  as additive [Fig. 9(a)], many spherical particles are seen on the surface of a dense body. With reference to the elementary compositions listed in Table III (i.e., spot A), these spherical particles are believed to be formed from melting of the Al particles, which were also seen to be partially oxidized. A few of more heavily oxidized Al particles are also seen in Fig. 9(a) (e.g., spot B). Below these distinct particles is a large and dense body, which is believed to be formed from melting and coalescence of Al particles. This is consistent with the observation that the reactant compact melted and collapsed after heating. In the cases of using  $\text{NH}_4\text{F}$ , urea, stearic acid, and succinic acid as additives, the compacts were seen to become highly porous and be composed of distinct particles [Figs. 9(b)–9(f)]. These particles all have eggshell-like skins, which are composed of fine particles and are quite separate from their

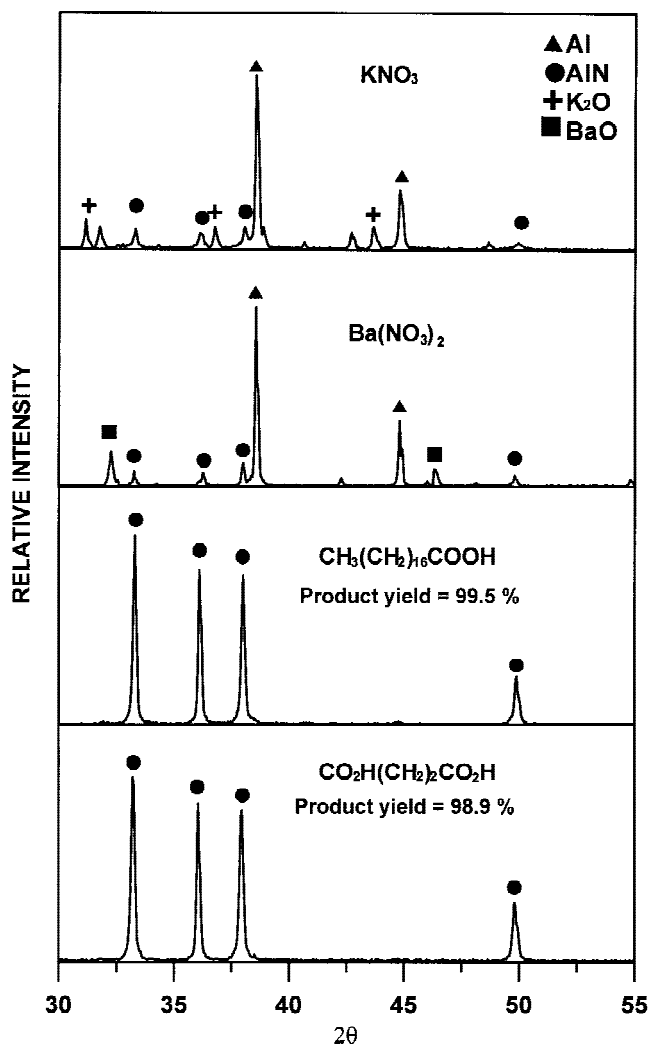


FIG. 7. XRD patterns of the products synthesized using additives containing neither  $\text{NH}_x$  nor X (Al:additive = 3:1; nitrogen pressure = 0.4 MPa).

interiors [Figs. 9(b) and 9(f)]. The elementary compositions listed in Table III suggest that the eggshell-like skins are mainly composed of nitrides and oxides of Al in the case of using  $\text{NH}_4\text{F}$  as additive [Fig. 9(b)]. When using urea as additive [Figs. 9(c) and 9(d)], the skins contain also carbon in addition to nitrides and oxides of Al. When using stearic acid and succinic acid as additives [Figs. 9(e) and 9(f)], the skins consist mainly of oxides and carbon. In all the cases, the interiors are mainly Al as suggested by the elementary compositions listed in Table III (spots I and L). Shown in Fig. 10 are SEM photographs of the fractured surfaces of the products synthesized using additives of (a)  $\text{NH}_4\text{F}$  and (b) urea. Many eggshell-like structures are clearly seen, indicating that the eggshell-like skins observed when heating the compacts under Ar atmosphere were indeed formed during the combustion synthesis reaction.

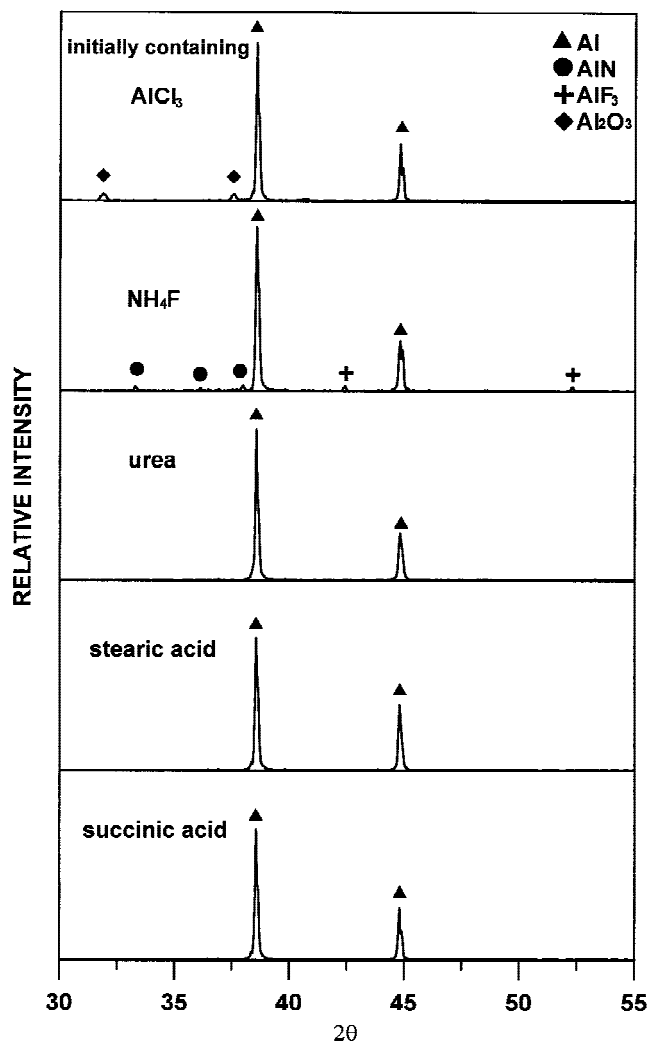


FIG. 8. XRD patterns of the compacts after being heated under Ar atmosphere for approximately 100 s (Al:additive = 3:1; nitrogen pressure = 0.4 MPa).

#### IV. DISCUSSION

Since the temperature during combustion is much higher than the melting point of aluminum, aluminum particles will melt before proceeding with the combustion reaction. As mentioned previously, when using a reactant compact composed of only Al particles (i.e., no additives), the compact melted and collapsed during heating. Although it could be ignited, the combustion reaction extinguished soon after ignition. When using such a reactant compact, the nitrogen available to the combustion reaction is limited to inside the pores because coalescence of Al particles inhibits nitrogen from diffusing into the compact. A high  $\text{N}_2$  pressure would thus be required to complete the combustion reaction and to achieve a high product yield.

Munir<sup>11</sup> calculated the  $\text{N}_2$  pressure required for combustion synthesis of AlN and other nitrides. By assuming that the available  $\text{N}_2$  is limited to inside the

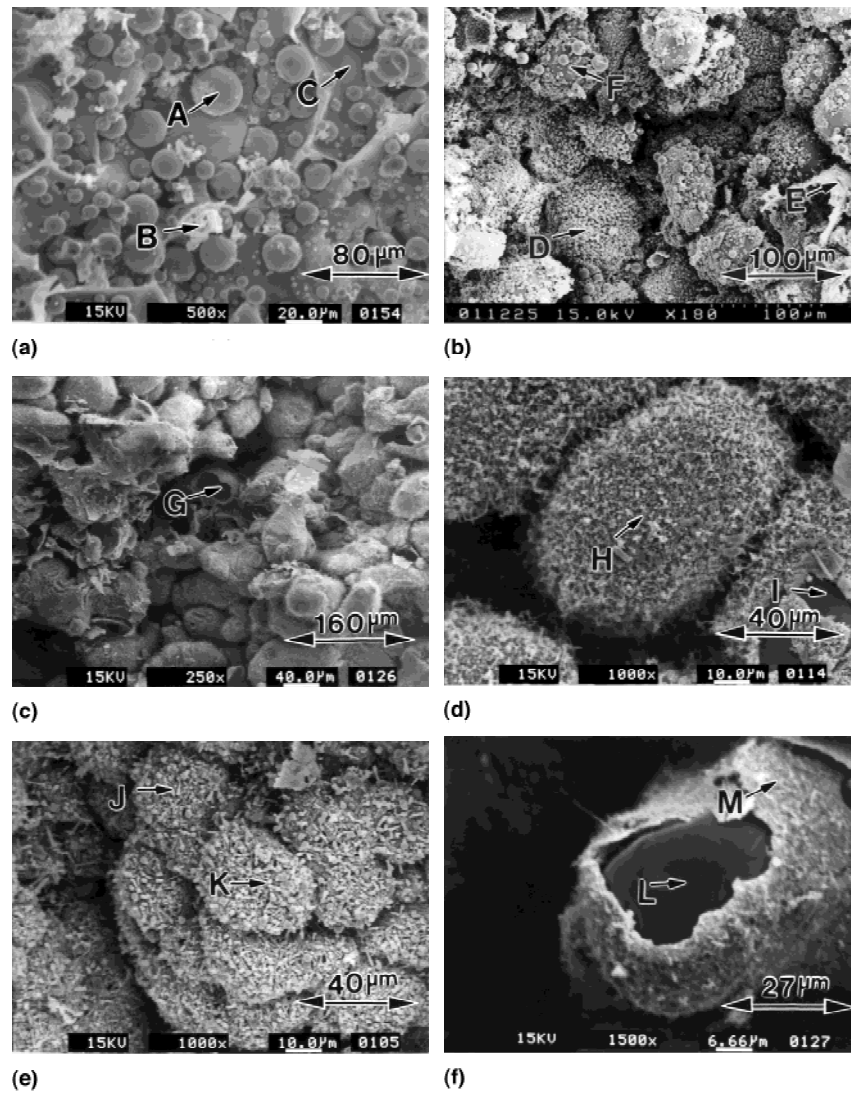


FIG. 9. SEM photographs of the fractured surfaces of the compacts after being heated under Ar atmosphere for approximately 100 s. Additives: (a)  $\text{AlCl}_3$ ; (b)  $\text{NH}_4\text{F}$ ; (c,d) urea; (e) stearic acid; (f) succinic acid (Al:additive = 3:1).

pores, he found that, for the synthesis of AlN, a  $\text{N}_2$  pressure of  $6 \times 10^3$  atm is required to achieve a product yield of 100% for a compact having a porosity of 0.5. Costantino and Firpo<sup>12</sup> studied the combustion synthesis of monolithic AlN by burning Al–AlN mixtures and found that a  $\text{N}_2$  pressure of 100 MPa or higher was required to achieve densified products with 80–95% of AlN mass fractions. Coalescence of Al particles not only limits the nitrogen availability but also reduces significantly the gas–solid (liquid) interface area, thus retarding greatly the combustion reaction. To obtain a high product yield with a low nitrogen pressure, coalescence of Al particles must be minimized during combustion reaction.

As described previously, when using  $\text{NH}_4\text{X}$ , urea, stearic acid, and succinic acid as additives, high product yields were obtained (Figs. 4–7) with a nitrogen pressure

TABLE III. Elementary compositions for the spots shown in Fig. 9.

Spots in Fig. 9	Elementary composition (wt%)					
	Al	N	O	C	F	Cl
A	80.2	1.1	13.4	5.1	0	0.2
B	64.5	0	30.2	3.7	0	1.6
C	74.1	2.4	16.8	1.4	0	5.3
D	61.6	25.1	8.8	1.5	2.9	0
E	38.9	3.6	42.8	11.6	2.2	0
F	55.2	29.7	12.4	2.7	0	0
G	47.8	14.9	18.0	19.3	0	0
H	52.4	15.1	13.7	18.8	0	0
I	87.1	8.4	2.4	2.1	0	0
J	57.3	3.5	17.9	21.3	0	0
K	44.6	4.7	10.7	40.0	0	0
L	94.3	0	4.5	1.2	0	0
M	55.3	0.3	27.6	10.8	0	0

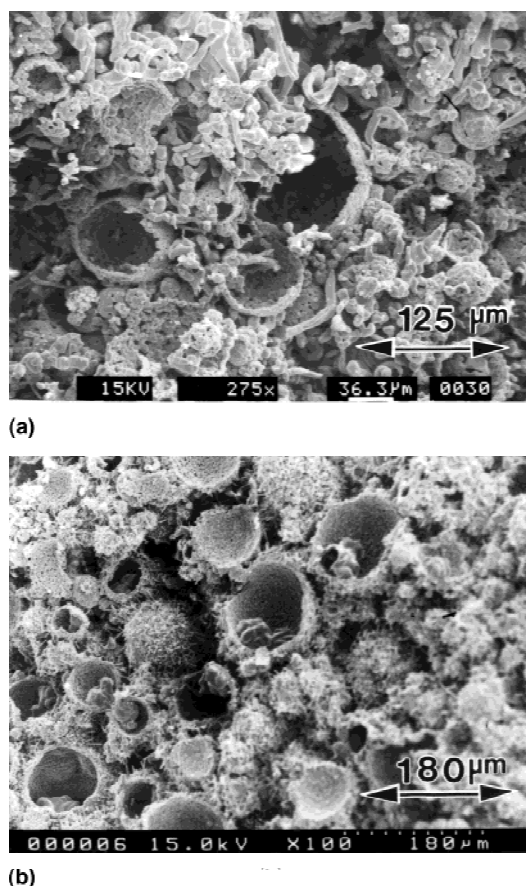


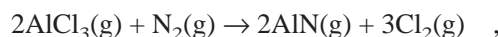
FIG. 10. SEM photographs of the fractured surfaces of the products synthesized using additives of (a) NH<sub>4</sub>F and (b) urea (Al:additive = 3:1; N<sub>2</sub> pressure = 0.4 MPa).

of 0.4 MPa (compared to  $6 \times 10^3$  atm and 100 MPa in other studies<sup>11,12</sup>). In these cases, the compacts were observed retaining their shapes during combustion reaction. The results of heating them under Ar atmosphere showed that the compacts not only retained their shape but also became highly porous after heating. These additives thus have two effects on the combustion reaction: First, they produce numerous pores inside the compact (by vaporizing, decomposing, or sublimating themselves). Second, they prevent the Al particles from coalescing. (Nitrogen could thus diffuse easily into the compact, resulting in high product yields.)

In contrast, when the reactant compacts contained the other compounds listed in Table I as additives, the compacts either could not be ignited [when containing NaN<sub>3</sub>, NaCl, KI, KNO<sub>3</sub>, and Ba(NO<sub>3</sub>)<sub>2</sub>] or had an incomplete combustion resulting in low product yields [when containing AlCl<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, and NH<sub>4</sub>HCO<sub>3</sub>]. To a more or less extent, these compacts all melted and collapsed during heating or combustion. Because of coalescence of the Al particles, diffusion of nitrogen was retarded, resulting in no ignition or incomplete combustion.

As listed in Table II (and also shown in Fig. 2 and 3), the compacts containing additives of NH<sub>4</sub>X and AlCl<sub>3</sub> required shorter ignition times and were ignited at lower temperatures than those containing CO(NH<sub>2</sub>)<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOH, CO<sub>2</sub>H(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H, and no additives. It is therefore believed that the additives of NH<sub>4</sub>X and AlCl<sub>3</sub> have catalytic effects on the combustion reaction. Furthermore, since the compacts containing CO(NH<sub>2</sub>)<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOH, and CO<sub>2</sub>H(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H have the same ignition time and the same ignition temperature as the compact containing no additives, these additives are believed to have no catalytic effects on the combustion reaction. Because NH<sub>4</sub>X and AlCl<sub>3</sub> all contain halogens and those additives containing only NH<sub>x</sub> [i.e., CO(NH<sub>2</sub>)<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, and NH<sub>4</sub>HCO<sub>3</sub>] have no catalytic effects, the catalytic effects are believed to be caused by halogens.

Nickel *et al.*<sup>13</sup> performed a thermodynamic and experimental study on AlN formation from AlCl<sub>3</sub> by chemical vapor deposition. According to their calculation, the nitridation reaction



is impossible under any temperature conditions because of a strongly positive  $\Delta G$  value. Besides, AlCl<sub>3</sub>(g) is thermally stable even at 1800 K and thus any essential breakdown of AlCl<sub>3</sub>(g) (to species e.g., AlCl<sub>2</sub>, AlCl, and Cl) in the temperature range of interest does not take place. They also pointed out that in the presence of Al, AlCl<sub>3</sub> can react with Al at temperatures  $\geq 1000$  K to produce AlCl<sub>2</sub> and AlCl, which can react easily with N<sub>2</sub> to form AlN. When using AlCl<sub>3</sub> as additive in the present study, AlCl and AlCl<sub>2</sub> (referred to as AlCl<sub>x</sub>) were generated (by reaction of AlCl<sub>3</sub> and Al) at the top surface of the compact during heating. Since AlCl<sub>x</sub> react more easily with N<sub>2</sub> than Al does, the combustion reaction was ignited at a lower temperature (i.e., a lower ignition temperature) and thus a shortest ignition time is required than when using no additives. AlCl<sub>3</sub> thus has a catalytic effect on the combustion reaction.

For the compacts containing NH<sub>4</sub>X, HX generated from their decomposition can react with Al to produce AlX<sub>x</sub> (i.e., AlX and AlX<sub>2</sub>). Again, the AlX<sub>x</sub> react more easily with N<sub>2</sub> than Al does. NH<sub>4</sub>X thus have a catalytic effect, enabling the compacts to be ignited at lower temperatures than those without any additives. (In these cases, the NH<sub>3</sub> from decomposition of NH<sub>4</sub>X may further decompose to N<sub>2</sub> and H<sub>2</sub> before ignition occurs). Since the combustion was ignited at lower temperatures, the combustion took place at temperatures (2000–2200 K) lower than when using additives with no catalytic effects such as urea, where the combustion temperatures were so high that the thermocouples were burned out. As



described previously, the combustion was observed to occur twice when using  $\text{AlCl}_3$  and  $\text{NH}_4\text{X}$  as additives. The nitridation reaction was apparently not complete during the first combustion due to the low combustion temperatures. A certain amount of Al was thus left, leading to the second combustion.

When the compacts containing  $\text{NH}_4\text{X}$  were heated under Ar atmosphere,  $\text{AlX}_x$  (generated by reaction of HX and Al) reacts with  $\text{NH}_3$  (or  $\text{N}_2$ , its decomposition product) to generate AlN. Since this reaction takes place in the gas phase, nucleation of AlN creates a huge number of fine particles.  $\text{AlX}_x$  will also react with  $\text{H}_2\text{O}$  (from the moisture absorbed on the reactant particles) to form fine particles of aluminum oxides. Deposition of the fine particles of the nitride and oxides is believed to be responsible for the formation of the eggshell-like skins surrounding the Al particles [Fig. 9(b)]. Because of the high melting points of the nitride and oxides, the eggshell-like skins prevent the Al particles from coalescing during heating and combustion. The compacts thus retain their porous structures throughout the combustion process, enabling the  $\text{N}_2$  to diffuse easily into the compacts and thus leading to high product yields.

When the compact containing  $\text{AlCl}_3$  is heated under Ar atmosphere, although  $\text{AlCl}_x$  could be formed by the reaction of  $\text{AlCl}_3$  and Al, neither  $\text{N}_2$  nor  $\text{NH}_3$  was available for the nitridation to form AlN. Instead,  $\text{AlCl}_x$  reacted with moisture to produce oxides as evidenced by the elementary analysis listed in Table III. Perhaps due to limited amounts of moisture, the oxide particles thus generated were apparently far from enough to form refractory skins on all the Al particles. The majority of the Al particles thus coalesced [Fig. 9(a)] leading to collapsing of the compact as observed during heating under Ar atmosphere. In the presence of  $\text{N}_2$ ,  $\text{AlCl}_x$  reacted with  $\text{N}_2$  and the AlN particles thus produced formed refractory skins on the Al particles. The production of the AlN particles was probably not fast enough because a slight melting and collapsing of the compact was observed during combustion. Consequently, a lower product yield was obtained as compared to the cases when using  $\text{NH}_4\text{X}$  as additives. During the heating stage, the presence of  $\text{NH}_3$  (i.e., when using  $\text{NH}_4\text{X}$  as additives) seems to accelerate the formation of AlN particles. A similar phenomenon was also observed by Kimura *et al.*<sup>14</sup> in their study on the synthesis of AlN by a floating nitridation technique. When a compact containing  $\text{CO}(\text{NH}_2)_2$ ,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , or  $\text{CO}_2\text{H}(\text{CH}_2)_2\text{CO}_2\text{H}$  is heated under Ar atmosphere, the surfaces of the Al particles were apparently oxidized by the additives as evidenced by the elementary analysis listed in Table III. Besides, fine carbon particles were generated due to decomposition of the additives. Oxidation of the Al surfaces and deposition of the carbon particles are believed to be responsible for the formation of the eggshell-like skins surrounding the Al

particles [Figs. 9(c)–9(f)]. Because of their high melting points, the eggshell-like skins prevented the Al particles from coalescing. The compacts containing these additives thus retained their porous structures throughout the combustion process, leading to complete combustion and thus achieving high product yields.

## V. CONCLUSION

Effects of various additives on the combustion process and the product yield for the combustion synthesis of AlN were investigated. Additives containing halogens were found to have a catalytic effect on the combustion reaction. This catalytic effect was attributed to the formation of  $\text{AlX}$  and  $\text{AlX}_2$ , which can react more easily with  $\text{N}_2$  than Al does. High product yields were obtained when using additives of  $\text{NH}_4\text{X}$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , and  $\text{CO}_2\text{H}(\text{CH}_2)_2\text{CO}_2\text{H}$ . In all these cases, eggshell-like skins were formed on the Al particles, consequently preventing the Al particles from coalescing. The compacts thus retain their porous structures throughout the combustion process, resulting in high product yields. The eggshell-like skins were believed to be formed by deposition of AlN, oxides, or carbon particles or by surface oxidation of the Al particles.

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