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Study of aluminum nitride formation by superfine aluminum powder combustion in air

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Abstract

An experimental study on the combustion of superfine aluminum powders (average particle diameter $a_s \sim 0.1$ μm) in air is reported. Formation of aluminum nitride during combustion of aluminum in air is focused in this study. Superfine aluminum powders were produced by wire electrical explosion (WEE) method. Such superfine aluminum powder is stable in air but, if ignited, it can burn in self-sustaining way. During the combustion, temperature was measured and actual burning process was recorded by a video camera. SEM, XRD, TG-DTA and chemical analysis were executed on initial powders and final products. It was found that powders, ignited by local heating, burned in two-stage self-propagating regime. The products of the first stage consisted of unreacted aluminum (~ 70 mass%) and amorphous oxides with trace of AlN. After the second stage AlN content exceeded 50 mass% and residual Al content decreased to ~ 10 mass%. A qualitative discussion is given on the probable mechanism of AlN formation in air.
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1. Introduction

Aluminum nitride has several unique properties as a ceramic material for electronic devices.[1] Conventional methods for synthesizing AlN powder are carbothermal reduction of Al$_2$O$_3$ powder, direct nitridation of Al metal powder and self-propagated high temperature synthesis (SHS).[2] All these methods used pure nitrogen as a nitriding reagent and the last two methods- aluminum powders of high purity (99.5%). One of new attractive low-cost method for AlN synthesis is combustion synthesis in air.[3–6]

Traces of AlN in final products of pure Al combustion in air were firstly reported in Boborykin's et al., theoretical study[3] and also proposed a thermodynamic explanation for formation of AlN and subsequent oxidation during combustion of Al in air.

Later, the phenomenon of the formation of a large amount of AlN (50 mass%) by combustion of layer of superfine aluminum powder (SFAP) in air was experimentally observed in the Ilyin and Proskurovskaya

work.[4] In that work authors have shown that more than 50 mass% of AlN (AlON) formed in combustion of a cone-like pile of ultrafine aluminum powder in air. But in that work the process of combustion was monitored by thermocouple only and the results of those work were semiqualitative.

Six years later Tsushida et al., have demonstrated the AlN formation in an experiment on combustion of mechanically activated aluminum and graphite mixtures in air.[5,6] They have activated micron-sized Al + C powders of different ratios (1/7–7/1) in the ball mill in an argon atmosphere. After such activation the powders Al + C (m $\sim$ 10 g) self-ignited immediately after their contact with air. Self-ignition results in burning in a two-stage regime (like SFAP without carbon)[4] with the presence of the high-temperature stage. In the opinion of Tsuchida et al., the mechanism of AlN formation includes the reaction of CO$_2$ formation and Al$_3$C$_4$ formation and nitridation.

Thus, these two cases[4–6] have the same final prime reaction product (AlN) and the burning regimes are similar. But what is the mechanism of AlN formation has not been investigated in detail until now. The main question is: why does nitrogen from the air react with aluminum instead of the oxygen present? In many AlN

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synthesis studies, if traces of oxygen appear, then AlN intensively reacted with oxygen[7] to form Al_2O_3.

In the present paper the experimental results with pure superfine aluminum powders combustion in air were considered in order to understand the formation of AlN in air. SFAP, average particle diameter ~ 0.1 μm, obtained by wire electrical explosion (WEE) method,[8] is not pyrophoric after slow air-passivation but can burn in self-propagating regime in air by local ignition. A possible mechanism of formation of AlN from gaseous intermediates is discussed and combustion process of the SFAP in air was comprehensively studied in this work.

2. Experiment

The SFAP was obtained by the WEE method in an argon atmosphere using the facilities developed by the High Voltage Research Institute, Tomsk, Russia. The specific surface area of SFAP, determined by nitrogen adsorption, was 10 m^2/g (Table 1). The aluminum metal content was $C_{Al} = 92$ mass%. The compositions of the initial SFAP and final combustion products were studied by XRD, chemical analyses using the Kjeldahl method (bound nitrogen content) and the volumetric method (aluminum metal content).[9] SEM images gave the structure of the initial powders and final products. A video camera was used to record the combustion process in situ. Temperatures were measured using both a W/Re thermocouple and optical pyrometer LOP-72. The thermocouple was placed in the center of the cone-like samples.

Four grams of superfine aluminum powder were poured onto a steel saucer (see Fig. 1). The shape of the powder sample was cone like. For three statistically studied SFAP samples of equal mass (4 g) the ignition temperature determined by pyrometer was 750 ± 100–820 ± 100 K. Local ignition was initiated by an elec-

Table 1
SF AP physical properties

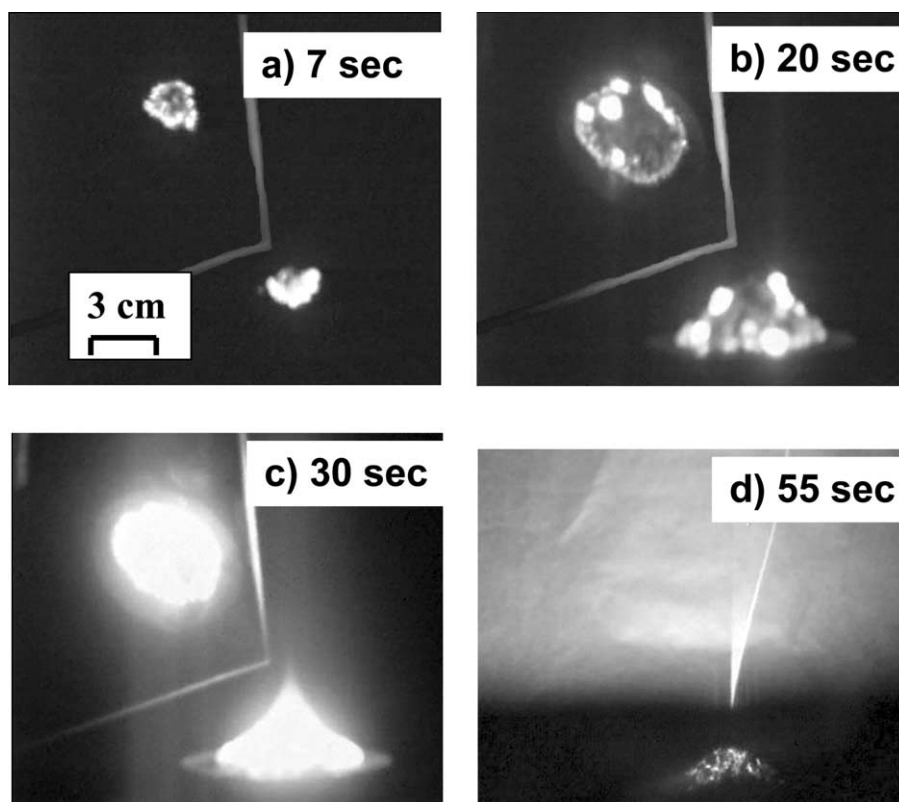| Specific surface area, m^2/g	Particle shape	Particle mean diameter, a_s, μm	Aluminum metal content, mass%	Apparent density, g/cm³
10.0	sphere	0.1	92.0	0.18

Fig. 1. Video images and reflections of burning of superfine aluminum powders (m = 4 g) in air: (a) ignition, (b) the 1st stage, (c) the 2nd stage, (d) cooling.

trically heated Ni–Cr alloy wire, which was placed at the top of the cone-like sample (Fig. 1a). After the ignition, combustion occurs as a non-stationary two-stage process. In is the first stage of combustion: from the ignition point, combustion waves of red color propagated through the surface of the sample (Fig. 1b). The maximal combustion temperature during stage 1 did not exceed 1400 ± 100 K (measured by pyrometer), but temperature increase during the first stage is not reflected on the temperature trace (Fig. 2) because the thermocouple was placed in the center of the conic sample and not sensitive for combustion through the surface of the conic sample. Spontaneously after a rather slow first stage a fast temperature increase up to 2500 ± 50–2800 ± 50 K (measured by thermocouple) was observed accompanied by bright radiation of a white color (stage 2). The second stage usually began from the center of the sample and then propagated through the full volume of the sample (Fig. 1c). After the second stage when the main part of the SFAP was reacted, the sample was cooled down fast (Fig. 1d).

XRD and chemical analysis showed that the homogenized product of the first stage, which was quenched by the fast placing to argon, consisted of unreacted aluminum and amorphous aluminum oxides with some traces of AlN (Fig. 3b) (bound nitrogen content $C_N = 0.5 \pm 0.3$ mass%, aluminum metal content $C_{Al} = 70 \pm 1.4$ mass%). It is noticeable that those XRD patterns of the initial SFAP (Fig. 3a) and the quenched products of combustion after the first stage in air (Fig. 3b) are similar to each other: the most intensive peaks belong to the Al phase. After the second stage of SFAP combustion, the content of aluminum metal in the homogenized final combustion products substantially decreased ($C_{Al} = 11.0 \pm 1.4$ mass%) and the content of bound nitrogen increased ($C_N = 18.2 \pm 0.3$ mass%). If all the nitrogen from air is assumed bound as AlN (Fig. 3c), the content of AlN should be $C_{AlN} = 61.4$ mass%. Microstructures of the initial SFAP and the 2nd stage combustion products are shown in Fig. 4. The spherical particles of the initial SFAP (Fig. 4a) completely changed their morphology during combustion: the final products consisted of needle-like polycrystals of micron and submicron size (Fig. 4b,c).

3. Results and discussion

The final products of SFAP combustion in air are formed under conditions of high temperature ~ 2800 K at the second stage of combustion (Fig. 2). The AlN (AlON) also forms during the second stage of the process (Fig. 3c). In this case the oxidation of aluminum nitride does not occur, which, apparently, is connected with the encapsulation of nitrides by Al_2O_3, which protect nitride from oxidation. The initial powders are agglomerates of sphere like particles, whose average diameter is substantially less than 1 μm (Fig. 4a). However, the products of combustion show a skeleton of a spongy structure (Fig. 4b). The structural fragments of this structure are elongated crystals with lengths of tens of micrometers and thickness up to 1 μm (Fig. 4b,c).

The presence of the AlN phase in the final products of SFAP combustion is one of the main features of SFAP combustion, which contradicts the thermodynamic calculations (the nitride must be further oxidized in air as in the case of the later slow heating at DTA-TG study, see Fig. 5). During some period of time the accumulation of AlN might be assumed due to the chemical binding of nitrogen. In this case the stabilization of the large quantities of AlN (more than 50 mass%) at high temperatures occur only under the encapsulation or fast cooling of the nitride: otherwise suboxidation of nitrides would occur. At low temperatures (first stage, $T < 1400$ K) the oxidation process proceeds due to the diffusion of the oxidizers through the layer of products as in the case of bulk aluminum. Such behavior at metals combustion in gaseous oxidizers is well known for SHS systems.[2] According to XRD analysis (Fig. 3b), after the first stage of combustion of the SFAP in air, the
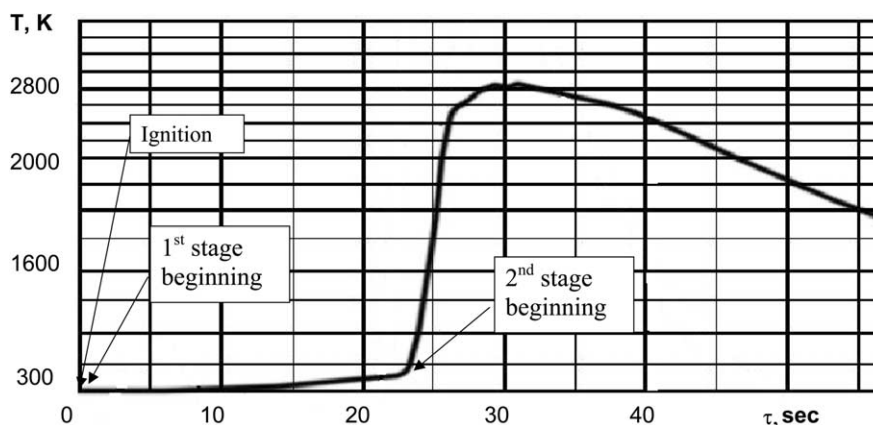

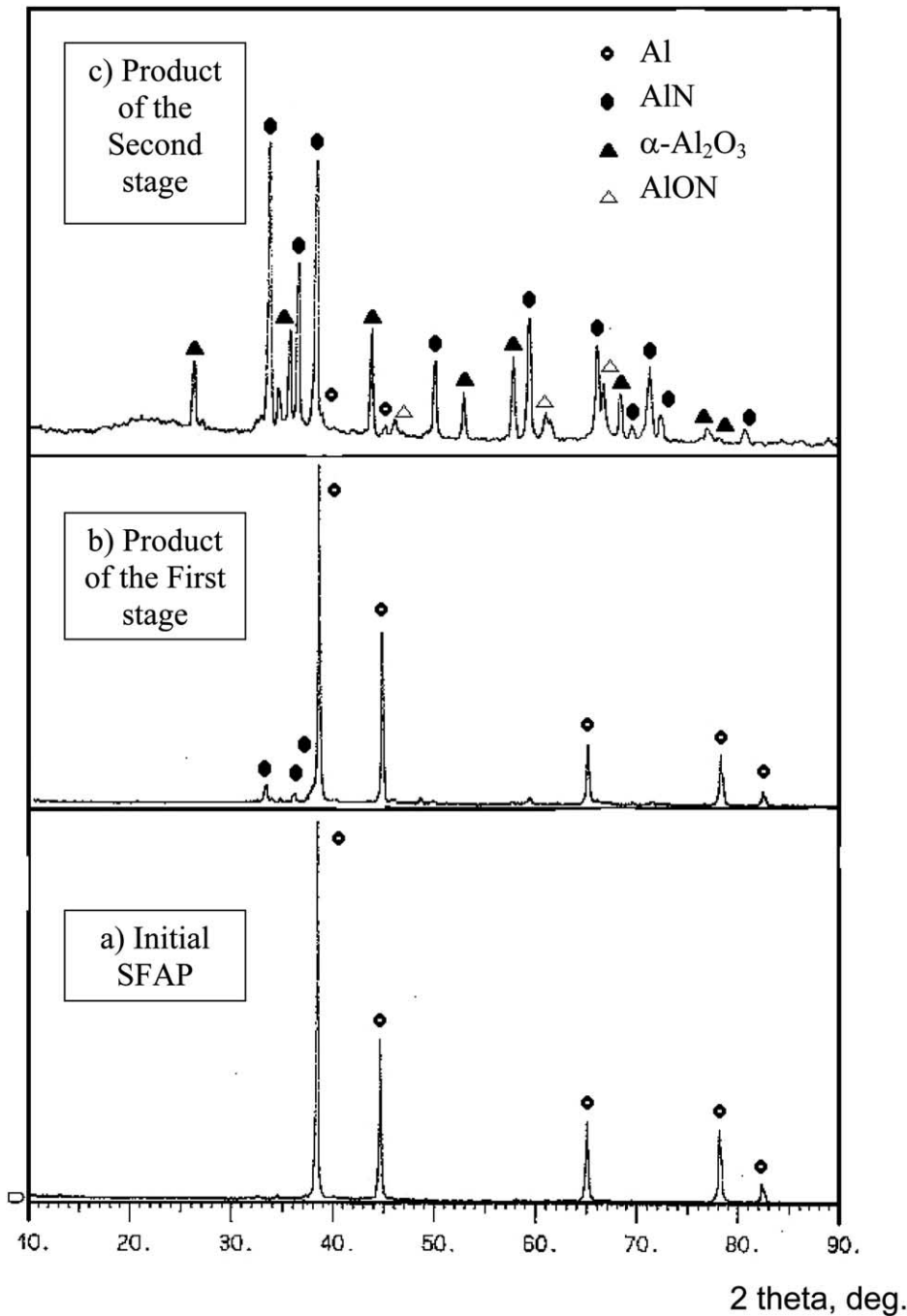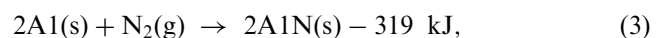Fig. 2. Temperature history of superfine aluminum powders (m = 4 g) combustion in air.
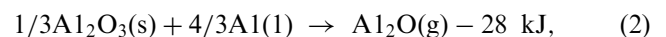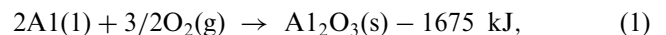
Fig. 3. X-ray diffraction patterns of initial superfine aluminum powder (a) and products of their combustion in air (b, c) (CuK$_\alpha$ irradiation, $\lambda = 1.54056$ nm).

main phase is unreacted aluminum. But according to the chemical analyses the quenched product of the first stage of combustion contain $C_N = 0.5 \pm 0.3$ mass% and $C_{Al} = 70 \pm 1.4$ mass%. It means that ~ 30 mass% belongs to amorphous oxides, which are not visible by XRD (Fig. 3b). On the other hand, the burning temperature of the samples achieves 1400 K during the first stage. Additionally, the volatility of Al_2O_3 increase in 2 times by melted aluminum presence[10] [see Eq. (2) below].

So, we can assume theoretically that the most significant role plays the following reactions during the first combustion stage:
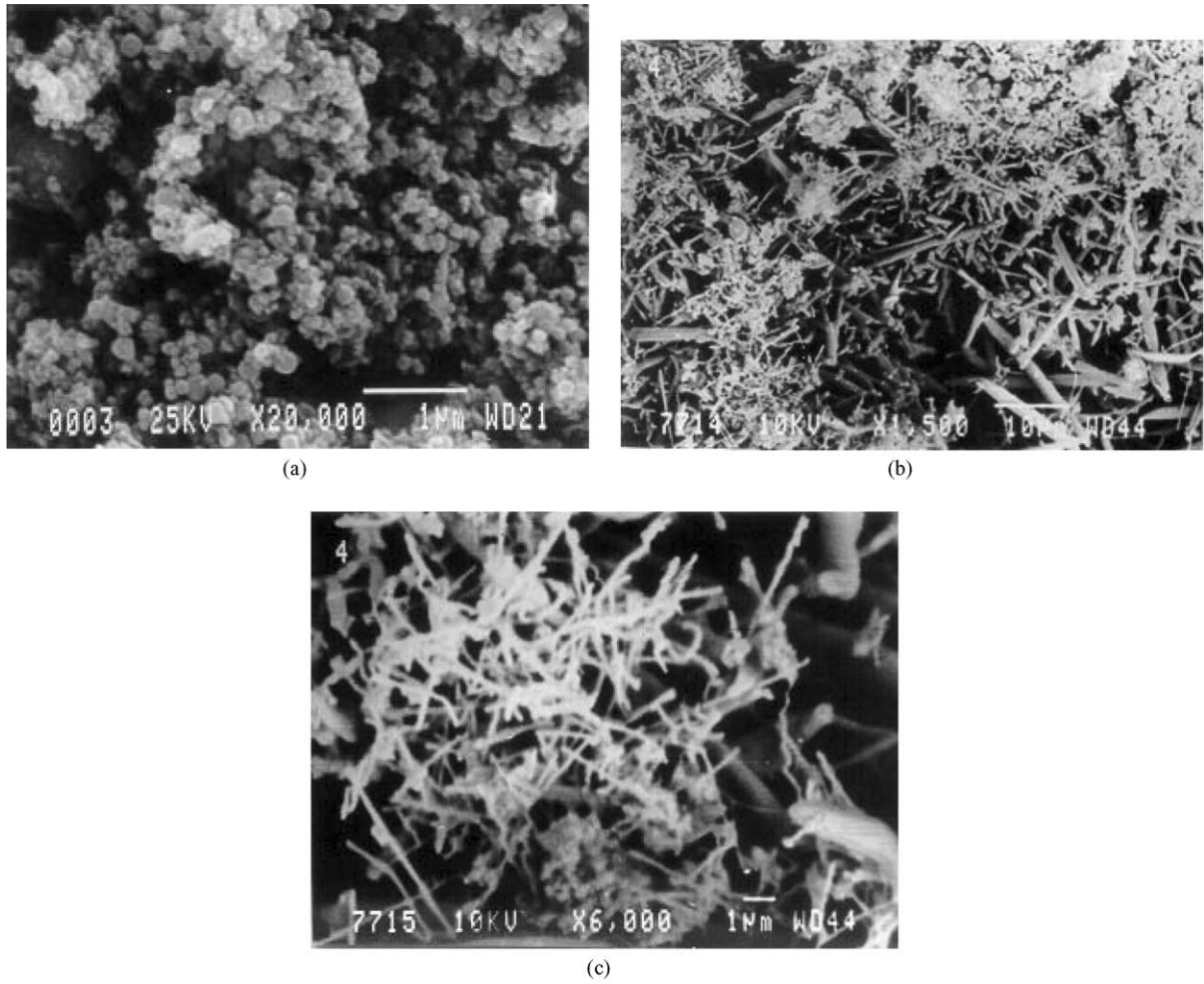
$$2Al(l) + 3/2O_2(g) \rightarrow Al_2O_3(s) - 1675 \text{ kJ}, \qquad (1)$$

$$1/3Al_2O_3(s) + 4/3Al(l) \rightarrow Al_2O(g) - 28 \text{ kJ}, \qquad (2)$$

$$2Al(s) + N_2(g) \rightarrow 2AlN(s) - 319 \text{ kJ}, \qquad (3)$$

Fig. 4. Scanning electron microscope images of initial SFAP (a, ×20000) and final products of their combustion in air (b, ×1500 and c, ×6000).
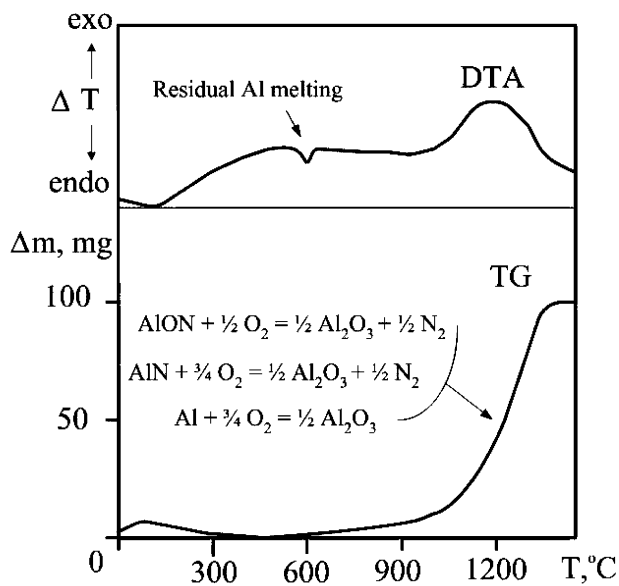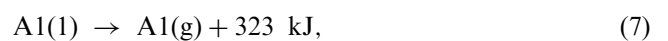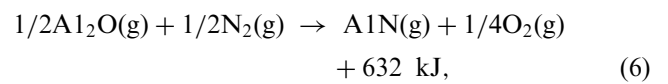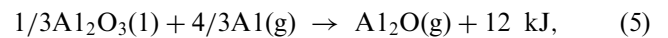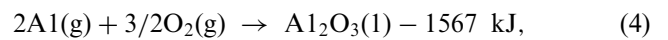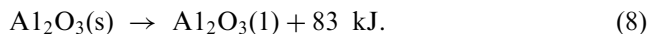

Fig. 5. DTA-TG study of final products of SFAP combustion in air (apparatus Q-1500 D, Hungary, heating rate 10 K/min, m = 300 mg, etalon α-Al$_2$O$_3$, atmosphere–air).

Thus, during the first stage of combustion, the amount of heat, which liberated at chemical reaction, is high enough for self-sustained combustion process. After the slow first stage of combustion the temperature of the sample rapidly increase up to 2800 K, most probable because of the change of combustion to gaseous intermediates oxidation and nitridation by the components of air. At high temperatures ($T \approx 2800$ K) it is necessary to consider the reactions:

$$2Al(g) + 3/2O_2(g) \rightarrow Al_2O_3(l) - 1567 \text{ kJ}, \tag{4}$$

$$1/3Al_2O_3(l) + 4/3Al(g) \rightarrow Al_2O(g) + 12 \text{ kJ}, \tag{5}$$

$$1/2Al_2O(g) + 1/2N_2(g) \rightarrow AlN(g) + 1/4O_2(g) + 632 \text{ kJ}, \tag{6}$$

$$Al(l) \rightarrow Al(g) + 323 \text{ kJ}, \tag{7}$$

$$Al_2O_3(s) \rightarrow Al_2O_3(l) + 83 \; kJ. \tag{8}$$

Thus, we assumed that aluminum nitride forms in the second stage of the combustion process through gaseous suboxides and than capsulate by Al_2O_3 or rapidly cooled. At low temperatures with heat liberation Al_2O_3, Al_2O and AlN are formed [Eqs. (1–3)]. But at high temperatures only the Al_2O_3 formation is exothermic [Eq. (4)]. The formation of AlN for the gas phase can be assumed to be in the endothermic reaction [Eq. (6)] at the second (high-temperature) stage of the SFAP combustion. Thus, for SFAP combustion in air, aluminum does not react with oxygen completely, but also forms nitride in the gas phase. In other words, in the case of SFAP combustion in air, there is a kinetic limitation on the thermodynamically possible process of AlN oxidation. Such kinetic limitation is possible due to AlN gas formation at 2800 K and immediate rapid condensation and cooling. The proposed reactions of AlN formation and stabilization are not contradicted to thermodynamics. The reactions are also different from the supposed by Tsushida et al., [5,6] chain of transformation in air:

$$Al \xrightarrow{\text{combustion(1 stage),C}} Al_3C_4 \xrightarrow{\text{combustion(2 stage),N}_2} AlN,$$
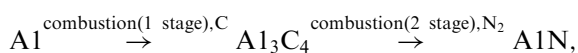
because there was no carbon in the initial SF AP studied in this work.

The formation and stabilization of nitrides during combustion of powdery elements in air is a normal feature not only for aluminum (present article) and boron[11] but also for zirconium.[12] It was recently discovered that during the oxidation of powdered lanthanum in air, the final products contained 50 mass% of LaN.[13]

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