

## Combustion of Al–Al<sub>2</sub>O<sub>3</sub> mixtures in air

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### Abstract

An experimental study on the aluminum oxynitride and aluminum nitride formation by combustion of mixtures of micron-sized aluminum powder (average particle diameter  $a_s \sim 9.0 \mu\text{m}$ ) and alumina nanopowder ( $a_s \sim 0.05 \mu\text{m}$ ) of the fixed mass ( $\sim 10 \text{g}$ ) and different mass ratios ( $\text{Al}/\gamma\text{-Al}_2\text{O}_3 = 0.1\text{--}19.0$ ) in air is reported. The formation of aluminum oxynitride ( $\text{Al}_3\text{O}_3\text{N}$ ) and aluminum nitride during the combustion of powdery aluminum-based mixtures in air is discussed in this study. The combustion synthesis of  $\text{Al}_3\text{O}_3\text{N}$  and AlN was carried out in self-sustaining way. XPS-FESEM, XRD and chemical analysis were executed on final products of synthesis. The combustion process was also recorded by a video-camera. It was found that powdery mixtures, ignited by local heating, burned in one- or two-stage self-propagating regime. The combustion regime is different for different initial mass ratios  $\text{Al}/\gamma\text{-Al}_2\text{O}_3$  and mainly depends on the content of fuel (aluminum powder) in mixture.

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### 1. Introduction

The AIONs are more resistive to oxidation<sup>1</sup> materials, than AlN. Additionally, they have more attractive properties than AlN in the electronic high-temperature devices. The industrial way for synthesis of AIONs of different compositions is high-temperature sintering of AlN and Al<sub>2</sub>O<sub>3</sub> in pure nitrogen or a vacuum.<sup>2</sup> Relatively novel method of  $\gamma$ -AION synthesis is carbothermal nitridation of Al<sub>2</sub>O<sub>3</sub>. Under the condition of  $\gamma$ -AION synthesis offered in Li's paper,<sup>3</sup> the sintering temperature was decreased down to 1600 °C. Li et al. have reported, that in their method the addition of less than 10 mass% of MgO and the following carbothermal nitridation of mixture (Al<sub>2</sub>O<sub>3</sub> + C) for 2 h results in the formation of the complete  $\gamma$ -AION phase: the reflexes of  $\gamma$ -AION are the most intensive in XRD patterns. However, Li's method of AION synthesis still required the very pure nitrogen (oxygen content: 7 p.p.m.), high-temperatures regimes (1600 °C) and MgO as a stabilizer. The mechanism of AION formation in carbothermal

reaction is well described in Bandyopadhyay et al.'s paper.<sup>4</sup> They established AION phase as intermediate in AlN carbothermal synthesis under the temperature higher than 1600 °C.

Another attractive low-cost method for AION synthesis is combustion synthesis in air.<sup>5</sup> The details for AlN synthesis under the similar experimental conditions were given in our work.<sup>6</sup> In that work four grams of superfine aluminum powder ( $a_s \sim 0.1 \mu\text{m}$ ) were poured onto a steel saucer and locally ignited. After the ignition, combustion occurs as a two-stage process. At the first stage of combustion from the ignition point combustion waves of red color propagated over the surface of the sample and inside the sample. The maximal combustion temperature during stage 1 did not exceed 1400 K. After a rather slow first stage a fast temperature increase up to 2500–2800 K was observed accompanied by bright radiation of a white color (stage 2). The second stage usually began at the center of the sample and then propagated through the whole volume of the sample. This type of combustion synthesis results in high content of AlN (up to 60 mass%) in the condensed combustion products. The novelty of this method lies in using air-as-nitridation-reagent for AlN synthesis, i.e. the pure nitrogen has not been used.

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In the present work we studied the process of Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mixtures oxidation and combustion in air in self-sustaining regime. The processes of AlON and AlN formation and subsequent oxidation are also discussed. The Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ratio for AlON synthesis in air was found as a result of such experiment and it is emphasized on this work.

## 2. Experiment

The initial raw materials were industrial micron-sized Al powder and nano-sized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (Table 1). All experiments on samples combustion were carried out in air at the room temperature of  $\sim$ 298 K and a relative humidity of  $\sim$ 75%. The compositions of the final combustion products were studied by XRD and chemical analyses using the Kjeldahl method (bound nitrogen content).<sup>7</sup> The phase identification was carried out with the aid of JCPDS diffraction data cards. XPS-FESEM images gave the structure and composition of the fragments of initial powders and final products.

The technique of the combustion synthesis in air was published in our previous paper and used in this study.<sup>6</sup> The preliminary mixed dry powders were poured onto a saucer made from hexagonal BN. Thus, the shape of the powder sample was cone like. For this work per each ratio Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> three statistically studied powdery samples of fixed mass ( $\sim$ 10 g) were taken. After the local ignition, combustion occurs as a non-stationary one- or two-stage process (Table 2). Combustion waves of red color propagated over the surface of the sample at the first stage of combustion (Fig. 1a) from the ignition point similar to superfine aluminum powder.<sup>5</sup>

Furthermore, we have observed a local flame tongues on the surface of cone-like sample (Fig. 1b). After the first stage a fast temperature increase was observed for samples nos. 4–9 (Table 2), accompanied by bright radiation of white color (stage 2, Fig. 1c). After the second stage the samples were cooled down fast (Fig. 1d). The increase of the content of Al in samples 1–3 resulted in an unstable “pulsatory” character of combustion origin and without high-temperature stage (white luminescence).

XRD and chemical analysis have shown that the homogenized condensed final products consisted mainly of unreacted aluminum (JCPDS 04-0787), aluminum nitride (JCPDS 25-1133), aluminum oxynitride (Al<sub>3</sub>O<sub>3</sub>N, JCPDS 36-0050) and aluminum oxide ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, JCPDS 46-1212) (Fig. 2). Initial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> completely transforms into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> even with one-stage combustion, e.g. the temperature of the first stage is higher than 1200 °C.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is the basic phase in the condensed products of mixtures Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 0.1–0.4. The combustion of mixtures with ratios Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 0.7 and 1.0 leads to AlON phase formation. AlN is stable in the range of initial ratios Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 1.5–4.0. The last two compositions (samples 9 and 10, Table 2) have shown that initial aluminum poorly reacted with air at high concentration of Al.

Bound nitrogen content in the homogenized final products changes from [N] = 0.2  $\pm$  0.1 mass% for Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 0.1 to [N] = 14.1  $\pm$  0.4 mass% for Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 2.3 (Fig. 3). It is noticeable, that the curve of AlN content (Fig. 2) repeats the curve of bound nitrogen content (Fig. 3). The morphology and XPS-spectrum of the synthesized AlON (at Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 1.0) is shown in Figs. 4 and 5 correspondingly. The

Table 1  
Main characteristics of the powdered raw materials

Powder	Origin				
	Impurities (mass%)	Average particle diameter ( $\mu$ m)	Metallic aluminum content (mass%)	Apparent density (g/cm <sup>3</sup> )	Particle shape
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Metal oxides, 1.1	0.05	1.5	0.06	Flake
Al	Amorphous Al <sub>2</sub> O <sub>3</sub> , 0.1	9.0	98.5	0.9	Sphere

Table 2  
Combustion characteristics for mixtures Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

Number of sample	Ratio Al/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Number of combustion stages	Features	Maximal intensity of phase in XRD pattern
	<0.1	No	Not initiated	
1	0.1	One	“Pulsatory” combustion	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
2	0.3			$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
3	0.4			$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
4	0.7	Two	Bright white radiation	Al <sub>3</sub> O <sub>3</sub> N
5	1.0			Al <sub>3</sub> O <sub>3</sub> N
6	1.5			Al <sub>3</sub> O <sub>3</sub> N + AlN
7	2.3			AlN
8	4.0			AlN
9	9.0			Al
10	19.0	One		Al
	>19.0	No	Not initiated	

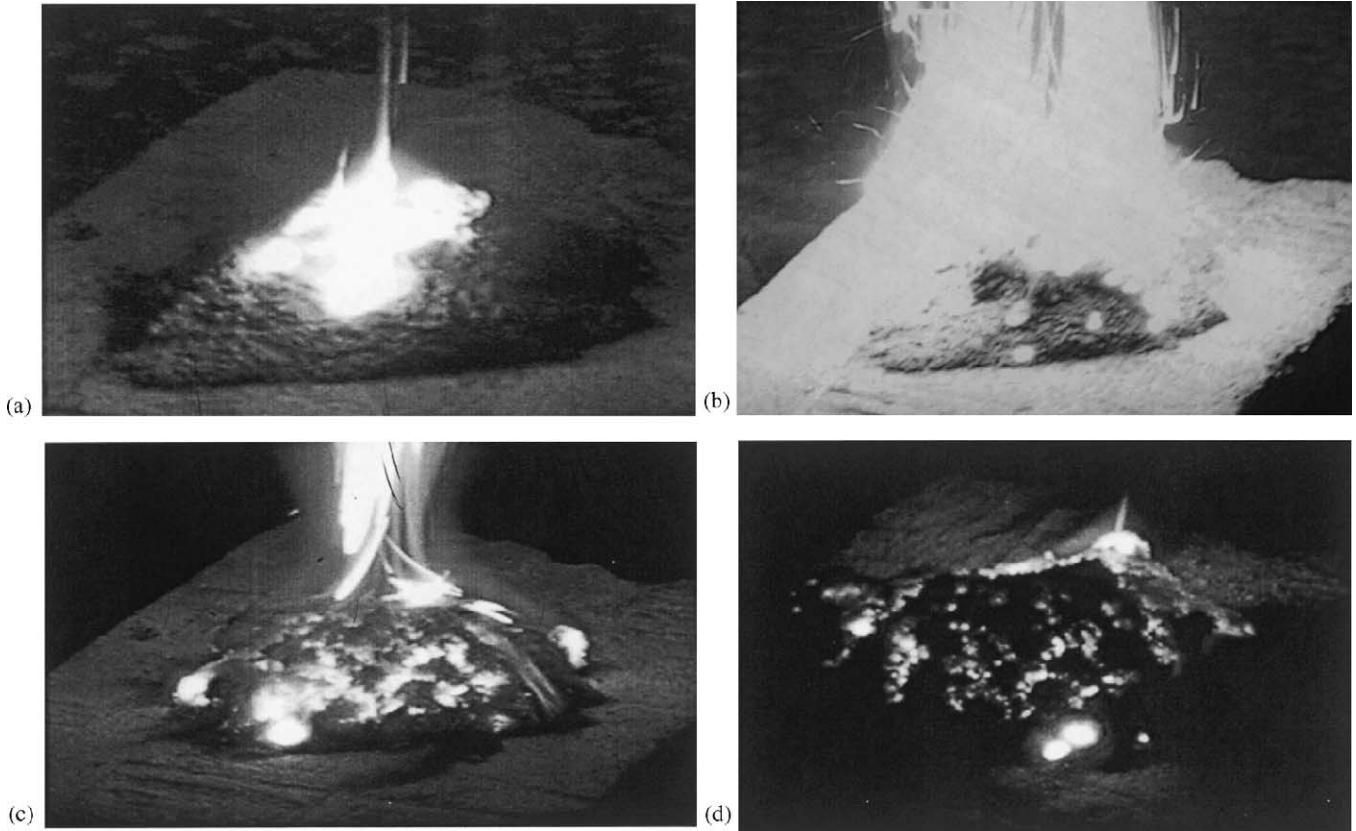


Fig. 1. Video images of the combustion process of mixture Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 1.0 in air (a: first stage, b: flame tongues, c: second stage, d: cooling).

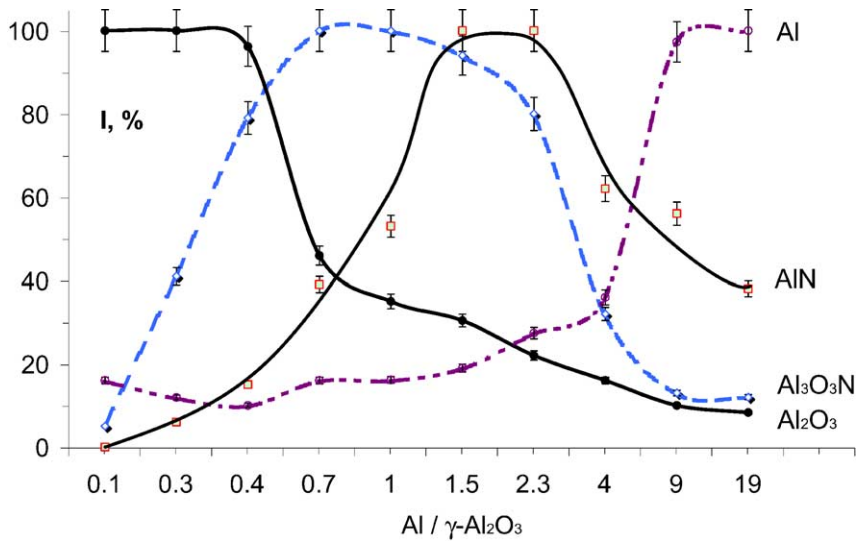


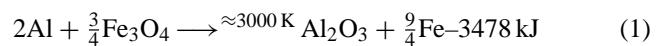
Fig. 2. Phase composition (XRD data, Cu K $\alpha$  irradiation,  $\lambda = 1.54056$  nm) of the final combustion products of mixtures Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in air.

high-temperature processes result in needle-like crystals formation, probably, through the liquid phase.

### 3. Results and discussion

The phenomenon of aluminum reaction with aluminum oxide without gaseous oxidizer (namely air) cannot be ex-

plained with thermodynamics only. For example, the aluminothermic strongly exothermic reaction (1) occurs at much higher rate and temperature.



Hence, the reaction of Al with aluminum oxide cannot be referred to this type of reactions. Probably, aluminum oxide

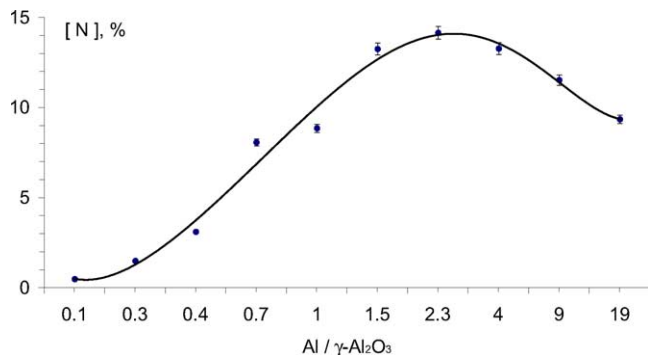
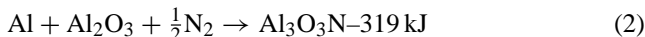


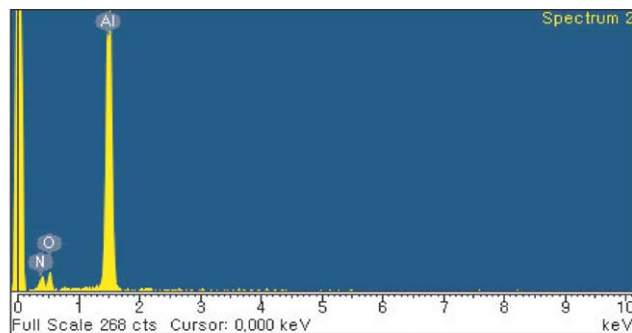
Fig. 3 Content of bound nitrogen in the final combustion products of mixtures Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in air.

reacts with melted aluminum formed as a result of aluminum oxidation by air.

During preliminary mixing large aluminum particles became covered with small Al<sub>2</sub>O<sub>3</sub> particles. At first, isolated aluminum particles ignited. The propagation of the combustion wave results in ignition of the majority of aluminum particles if assume that heat of combustion goes through the layers of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ignites new portions of aluminum particles. Additionally, isolation layer, consisting of aluminum oxide, prevent aluminum drops from coalescing before the combustion wave comes. Within the certain range of Al concentration (Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 0.7–1.5) the reaction of liquid aluminum with nitrogen (2) become more significant.



Aluminum oxynitride formation in the combustion process is confirmed by XPS data (Fig. 5). However, the content



Standard :  
 N Si3N4 1-Jun-1999 12:00 AM  
 O SiO2 1-Jun-1999 12:00 AM  
 Al Al2O3 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
N K	13.52	17.14
O K	25.60	37.08
Al K	60.88	45.78
Totals	100.00	

Fig. 5. XPS spectrum for the needle crystallite of final combustion products of mixture Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 1.0 in air.

of nitrogen (by XPS data, Fig. 5) is lower than stoichiometric one, e.g. the external surface layer of the needle crystals lack nitrogen.

Final products of aluminum combustion with small additives of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> looked like cakes. Aluminum drops (with the diameter of 0.5–1 mm) are visible inside the cakes of combustion products. For these samples the processes of aluminum melting and coalescing play a significant role during the combustion. The content of the metallic Al for these samples is

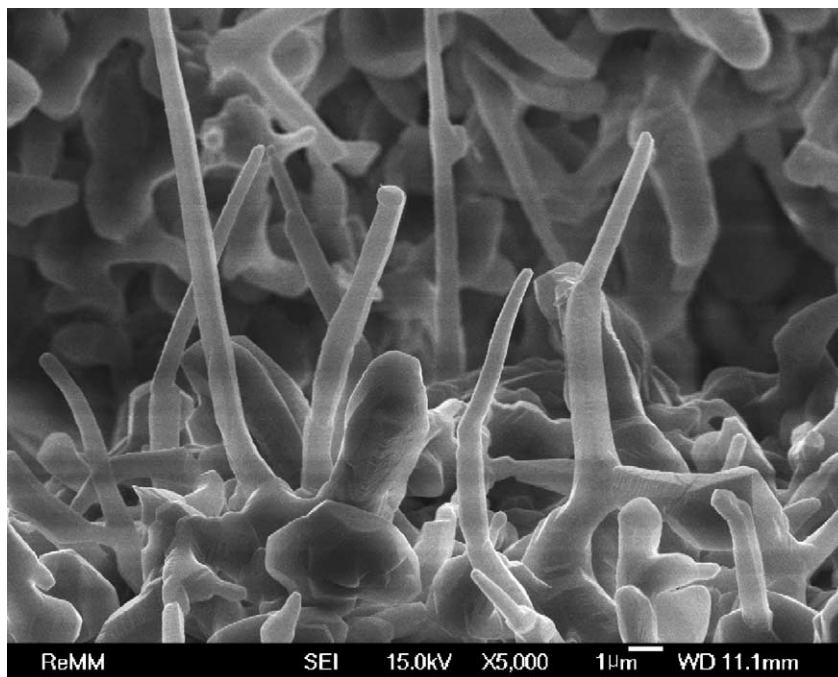


Fig. 4. Scanning electron microscope image of the final combustion products of mixture Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 1.0 in air (5000 $\times$ ).

maximum (Fig. 2). However, for the mixtures Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 2.3–4.0 the content of Al at the end combustion products sharply reduce and for the samples with the smaller Al concentration that was minimum: the last ratio was Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 4.0, where the degree of aluminum transformation by combustion being high.

Thus, to sum up the experimental observation, the most probable mechanism of AlO<sub>3</sub>N<sub>3</sub> synthesis in the combustion wave is as follows. At the first stage of mixtures combustion, aluminum oxidation by atmospheric oxygen yields heat enough for aluminum to melt. The first stage is quite slow and aluminum reacts only with oxygen according to diffusive mechanism. Then aluminum melt reacts with nitrogen (2nd stage) and the melted aluminum oxide sinters with AlN to form Al<sub>3</sub>O<sub>3</sub>N. The second stage is a very fast process and the reaction zone is very narrow to prevent Al<sub>3</sub>O<sub>3</sub>N from further oxidation.

#### 4. Conclusion

The combustion of the mixtures of micron-sized Al powder and nanopowders of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in air occurs in one- or two-stage regime similar to superfine aluminum powder combustion without additives.<sup>6</sup> The range of ratios Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = 0.7–1.5 for aluminum oxynitride (Al<sub>3</sub>O<sub>3</sub>N namely) is de-

termined. By changing the combustion behavior of mixtures (ratio Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) it is possible to obtain AlON or AlN as one of the dominant phase in the final combustion products. The mechanism of the synthesis of AlN (AlON) during the combustion of mixtures, apparently, is correspond to that of superfine aluminum powders:<sup>6</sup> the combustion regime and composition of end products in particular.

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