Combustion of Ultrafine Aluminum in Air

A. P. Il'in,[1] A. A. Gromov,[1] V. I. Vereshchagin,[1] E. M. Popenko,[2] V. A. Surgin,[2] and H. Lehn[3]

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The paper reports results of studying the combustion of ultrafine aluminum (surface average diameter of particles is ≈ 0.1 μm) in a sealed bomb at an initial air pressure of 1 atm. The combustion proceeds in two stages, similarly to combustion in air. It is shown that during the two-stage combustion of ultrafine aluminum powder in the bomb, the mass concentration of chemically bound nitrogen in the final products increases by $\approx 20\%$ in terms of aluminum nitride. An increase in nitrogen content in confined combustion validates the previously proposed mechanism of binding air nitrogen with participation of the gas phase during aluminum combustion.

INTRODUCTION

The stagewise nature of combustion of aluminum powder and other metals has long been observed [1], and the combustion mechanism proposed in [2] explains many features of this phenomenon. Nevertheless, the nature of the combustion stages is still of considerable interest [3]. We note that combustion of metal powders in various gas media (air, mixtures of air with inert gases, etc.) proceeds in two or more stages. In the case of coarsely dispersed powders, preheating is required for self-sustaining combustion regimes. The ignition temperature for ultrafine powders (UFP) does not exceed $500°C$, and the two-stage combustion of ultrafine aluminum powder (UFAP) results in stabilization of more than 50% (by weight) nitrides and oxynitrides in the final products [4]. In the case of one-stage combustion, the final products of the same UFP contain only trace amounts of bound nitrogen. Tsushida et al. [5] found that aluminum nitride forms in the combustion of a pyrophoric mixture of aluminum and graphite powders in air. However, in some papers on aluminum powder combustion in air [1–3], the participation of nitrogen was ignored.

The efficiency of binding of air nitrogen can be increased using catalysts. It is known that transition metals play an important role in low-temperature binding of air nitrogen [6]. In [7], an attempt was made to increase the content of bound nitrogen in the final combustion products of UFAP by means of additives. Ultrafine powders of Cu, Ni, Fe, Sn, W, Mo, Si, C, and B, each in an amount of 9%, were mixed mechanically with dry UFAP (sample weight 4 g). Combustion was initiated by local heating of samples by a Nichrome wire. Addition of ultrafine powders of Cu, Ni, Si, C, and B had almost no effect on the content of bound nitrogen: the nitrogen content in the final products of UFAP combustion varied from (53.0 ± 0.6) to $(55.8 \pm 1.7)\%$ in terms of AlN [cf. $(53.4 \pm 0.5)\%$ for UFAP without additives]. The addition of an UFP of Sn decreased the content of bound nitrogen to $(29.2 \pm 0.6)\%$ in terms of AlN. The addition of UFP of Fe, Mo, and W led to an increase in the content of bound nitrogen (by 5.6–13.3% in terms of AlN). The effect of these additives is explained by an increase in combustion temperature for the mixtures. The effect of addition of 0.05–1.6% palladium acetate $PdAc_2$ (combustion catalyst of high-energy composite systems) on the process and products of UFAP combustion in air was studied in [8]. The addition of $PdAc_2$ has no effect on the content of bound nitrogen in the combustion products and, hence, $PdAc_2$ is probably not involved in the combustion process at any stage. Combustion of UFAP in air results in the formation of ultrafine powders ($S_{sp} \approx 1$ m^2/g), which begin to oxidize

[1]High-Voltage Institute, Tomsk Polytechnical University, Tomsk 634050; admin@admin.hvri.tpu.edu.ru.
[2]Biisk Technological Institute, Altai State Technical University, Biisk 659305.
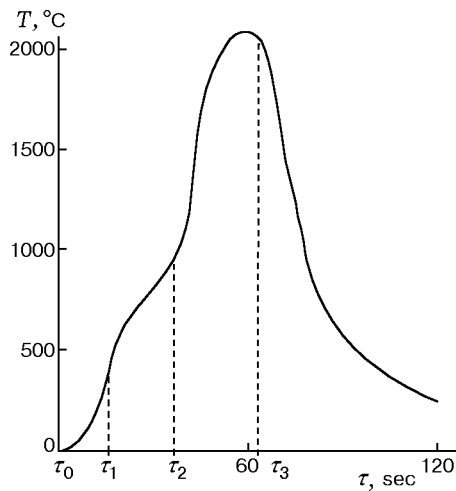[3]D.L.D. International, Paris, France.

Fig. 1. Typical curve of maximum sample temperature versus time of combustion: region τ_0–τ_2 refers to the first stage and region τ_2–τ_3 refers to the second stage.

Fig. 2. Line x-ray photographs of the products of UFAP combustion in the sealed bomb (a) and in open air (d is the distance between the planes).

at 660°C under reheating: oxidation of residual aluminum and final oxidation of aluminum nitride occur. At the same time, conditions of AlN synthesis involve heating to 2200–2400°C. Considering the fact of AlN stabilization (more than 50% by weight), we made an assumption on its encapsulation. The results obtained refer to the new phenomenon: synthesis of nitride in the presence of oxygen. Other methods of AlN synthesis do not use an oxygen-containing medium.

Thus, the additives catalyzing combustion affect only slightly the formation of nitrides and the mechanism of UFAP combustion. At the same time, it is known that the combustion processes involving gaseous reagents and intermediate products depend strongly on ambient pressure. The present paper reports results from investigation of confined combustion of UFP in a sealed steel bomb. The goal of this work was to study the effect of reduced air pressure on the nitride formation mechanism during the combustion process.

EXPERIMENT

Thermocouple measurements during UFAP combustion (5/20 W/Re thermocouple with a ceramic casing) showed that binding of air nitrogen occurs at the second combustion stage (Fig. 1). After completion of the first stage, the mass concentration of bound nitrogen in the final combustion products determined by the Kjeldahl method does not exceed 0.5%. The characteristic time of the spontaneous second stage is 30–40 sec (the time of cooling is ignored). The total increase in sample weight is 30% for a rate of nitrogen binding of about $3.3 \cdot 10^{-3}$ g/sec per 1 g of the starting UFAP. The
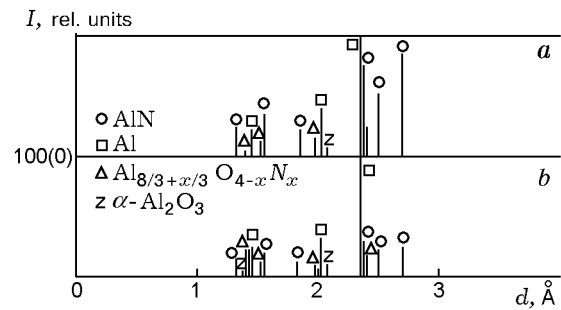
unoxidized aluminum content in the final products does not exceed 8–10%. The formation of aluminum nitride as an independent phase suggests a separate stage of its synthesis. The fact that air contains more nitrogen than oxygen led us to the assumption that the bound nitrogen content in the final combustion products can be increased by limiting the amount of oxygen or by confined combustion. In the experiments, we used a steel bomb with a volume of 3.43 liters. The initial pressure in the sealed bomb was nearly atmospheric. The powder samples were ignited by a Nichrome wire through which a current pulse was passed. Table 1 shows experimental results.

According to the results obtained, the limitation of access for oxygen increases the content of bound nitrogen (by 13.2% in terms of AlN). An x-ray phase analysis of the final products showed that the relative intensity of the reflections of the aluminum nitride phase is higher in the confined combustion than in combustion under conditions of free access for oxygen (Fig. 2). The experimental result — an increase in AlN content during confined combustion of UFAP at an initial pressure of 101.8 kPa — is not obvious. A decrease in pressure should result in rapid decay of the process: stable burning of the UFAP occurs only at pressures of $\approx$203 kPa or higher. It is known that a decrease in pressure facilitates gas-phase reactions. A decrease in pressure in the confined combustion resulted in an increase in AlN content in the final products. If the formation of AlN took place in the condensed phase, the yield of AlN would decrease according to the theory of self-propagating high-temperature synthesis [5]. Thus, the experimentally observed increase in the yield of AlN during UFAP combustion at decreasing pressure suggests the formation of the gas-phase nitride and its subsequent condensation. We note that the α-Al_2O_3 content in the products is higher in confined combustion than in combustion with free access for oxygen. However, x-ray phase analysis data do not show a substantial difference in the residual aluminum content in the examined samples (see Fig. 2).

TABLE 1

Comparative Results of Burning UFAP in Open Air and Closed Volume

Experimental conditions	m_s, g	m_a, g	Al/air	c_{AlN},%	Δm,%
Bomb	2.00	4.40	1.00/2.20	50.7	34.5
Air	2.00	∞	$1.00/\infty$	37.5	30.5

Notes. The bomb has a volume of 3.43 liters and the initial pressure is 101.8 kPA; m_s is the sample weight, m_a is the weight of air in the bomb, c_{AlN} is the mass concentration of AlN in the combustion products, and Δm is the increase in mass during combustion.
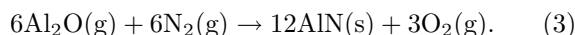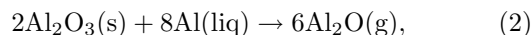
Results of differential-thermal analysis show that the products of combustion in the bomb are less stable in air: their oxidation rate is higher than that of the products obtained by combustion with free access for air. An increase in the weight of the final combustion products occurs during oxidation of both residual aluminum and aluminum nitride.

Previously, we studied the dependence of the bound nitrogen content during UFAP combustion in air on the sample weight. It was established that with increase in sample weight from 0.25 to 30 g, the AlN content in the combustion products increased. In the experiment, a maximum AlN content was not obtained. In the case of confined combustion in a sealed bomb (bomb volume 2.235 liters), with increase in the weight of the UFAP samples, the AlN content first increased and then decreased. Table 2 shows the experimental results. The AlN content in confined combustion was 17.8% higher than that in combustion of a control sample weight of 5.0 g under conditions of free access for oxygen. According to the results obtained, the content of unburned metallic aluminum was antibate to the dependence of the AlN content on the UFAP sample weight: the minimum was observed for sample No. 3. We note that the confined combustion of UFAP results in a considerable decrease in residual-gas pressure. With increase in UFAP sample weight from 0.1 to 7.0 g, the pressure in the bomb decreased from 101.3 kPa (atmospheric pressure) to 61.4 kPa. This affected both the first and second stages of the UFAP combustion.
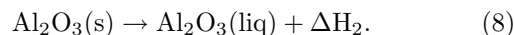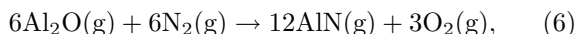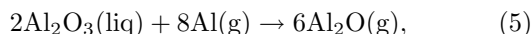
DISCUSSION OF RESULTS

The presence of small amounts of bound nitrogen in the products of aluminum combustion in air is normal because air contains $\approx 80\%$ nitrogen. From the viewpoint of thermodynamics, the probability of the formation of oxynitride, a compound indicating the presence of the both oxidizers, is high. A semi-quantitative study [3] showed that the final products of aluminum combustion in air contain 3–5% bound nitrogen with respect to bound oxygen. The presence of the independent AlN phase in the final combustion contradicts thermodynamic calculations (nitride should fully oxidize in air) and suggests that in a local powder region or at a certain time, only the nitride is accumulated as a result of chemical binding of nitrogen. This process is characterized by stabilization of large amounts of AlN (more then 50%), i.e., at high temperatures, the nitride is encapsulated; otherwise it would further oxidize. At low temperatures ($T \approx 293$ K), oxidation occurs by diffusion of the oxidizers through the product layer, and the decrease in the bomb pressure should result in a decrease in the rates of reactions (1) and (3):

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s), \qquad (1)$$

$$2Al_2O_3(s) + 8Al(liq) \rightarrow 6Al_2O(g), \qquad (2)$$

$$6Al_2O(g) + 6N_2(g) \rightarrow 12AlN(s) + 3O_2(g). \qquad (3)$$

At high temperatures ($T = 2800$ K), reactions (7) and (8) must be taken into account:

$$4Al(g) + 3O_2(g) \rightarrow 2Al_2O_3(liq), \qquad (4)$$

$$2Al_2O_3(liq) + 8Al(g) \rightarrow 6Al_2O(g), \qquad (5)$$

$$6Al_2O(g) + 6N_2(g) \rightarrow 12AlN(g) + 3O_2(g), \qquad (6)$$

$$Al(liq) \rightarrow Al(g) + \Delta H_1, \qquad (7)$$

$$Al_2O_3(s) \rightarrow Al_2O_3(liq) + \Delta H_2. \qquad (8)$$

A decrease in pressure during combustion results in inhibition of reactions (4) and (5) and acceleration of reactions (6)–(8). Thus, loss of the main heat source occurs and the combustion temperature decreases. The 17.8% increase in aluminum nitride content is obviously associated with the "margin of temperature" and sufficient amount of air in the bomb (sample No. 3). Apparently, even for the next sample, the amount of air was insufficient, which led an increase in residual aluminum content (sample No. 4, see Table 2).

Figure 3 shows a diagram of the thermodynamic state of the initial, intermediate, and final products of aluminum combustion in the presence of two oxidizers (nitrogen and oxygen). An analysis of this diagram shows that the only heat source at high temperature (2800 K) is the reaction of aluminum oxidation to Al_2O_3 (formation of AlN in the gas phase is

TABLE 2

Results of Confined Combustion of UFAP
(bomb with a volume of 2.235 liters and an initial pressure of 101.3 kPa)

Sample No.	m_s, g	Al/air	$\tau_2 - \tau_0$, sec	$\tau_3 - \tau_2$, sec	c_{AlN}, %	c_{Al}, %	p_{fin}, kPa	$p_{ini} - p_{fin}$, kPa
1	0.1	1/26.9	3.2	4.9	34.8	16.8	100.6	0.7
2	0.3	1/9.0	3.0	12.8	42.9	14.2	99.1	2.2
3	0.5	1/5.4	3.3	19.3	53.0	9.7	97.3	4.0
4	1.0	1/2.7	3.2	20.6	47.2	13.2	94.4	6.9
5	3.0	1.1/1	4.3	41.7	48.9	14.7	81.0	20.3
6	5.0	1.9/1	6.9	51.0	45.7	18.7	70.3	31.0
7	7.0	2.6/1	12.7	64.2	42.1	20.6	61.4	39.9

Note. p_{ini} and p_{fin} are the initial and final pressures, respectively.
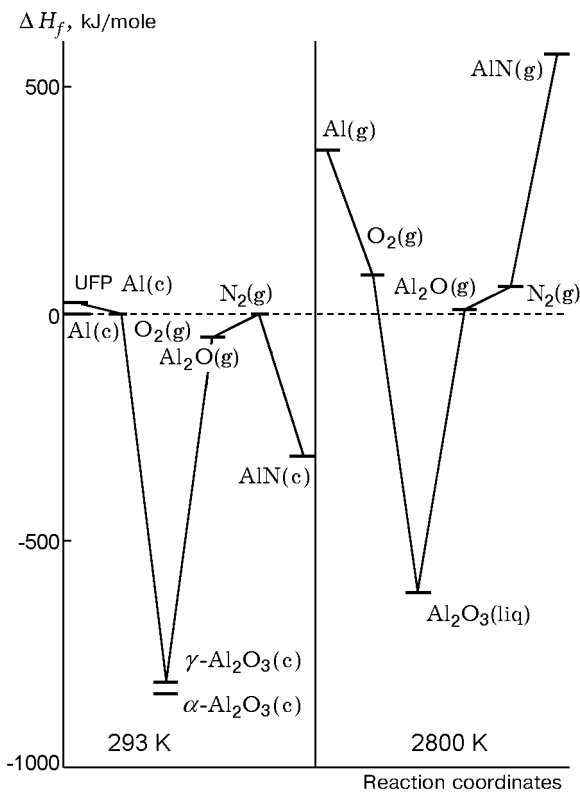
Fig. 3. Diagram of formation of the nitride phase in aluminum oxidation in air.

The results obtained suggest that gas-phase AlN is produced by an endothermic reaction at the second (high-temperature) stage of combustion (see Fig. 3). This is accompanied by two mutually exclusive effects occur: an increase in combustion rate and temperature and a simultaneous decrease in heat effect. The enthalpy of AlN formation is approximately 2.5 times smaller than the enthalpy of Al_2O_3 formation.

Confined combustion of UFAP leads to an increase in the AlN content in the final products. This can be caused by a decrease in the chamber pressure and displacement of equilibrium according to the Le Chatelier–Brown principle of formation of gaseous products (Al_2O and AlN). Under the conditions of the present experiment, liquid AlN does not exist: the gas is condensed to form the solid state, whereas Al_2O_3 is formed from the liquid state. It is possible that exactly the high temperature and localization of the oxidation process with subsequent formation of aluminum suboxide determine the nitride formation process. Thus, under certain conditions of UFAP combustion in air with excess of oxygen, aluminum forms gas-phase aluminum nitride rather than reacts with oxygen.

The formation and stabilization of nitrides during combustion of elementary powders in air is typical not only of aluminum, boron, titanium, zirconium, and silicon but also of other elements. Recently, it has been found that in oxidation of lanthanum powder in air, the final products contain $\approx 50\%$ lanthanum nitride [10].

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an endothermic process). The formation of gas-phase AlN at 2800 K is accompanied by heat absorption: $\Delta H_f^{2800\text{ K}}(\text{AlN}_g) \approx 585$ kJ/mole [9]. After formation in the gas phase (see Fig. 3), AlN is condensed at lower temperatures with heat release. Thus, at low temperatures, Al_2O_3, Al_2O, and AlN are formed with heat release.

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