

Kinetic and Thermodynamic Features of Combustion of Superfine Aluminum Powders in Air

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Abstract An experimental study on the combustion of superfine aluminum powders (average particle diameter, a_p : $\sim 0.1 \mu\text{m}$) in air is reported. The formation of aluminum nitride during the combustion of aluminum in air and the influence of the combustion scenario on the structures and compositions of the final products are in the focus of this study. The experiments were conducted in an air (pressure: 1 atm). Superfine aluminum powders were produced by the wire electrical explosion method. Such superfine aluminum powder is stable in air but once ignited it can burn in a self-sustaining way due to its low bulk density ($\sim 0.1 \text{ g/cm}^3$) and a low thermal conductivity. During combustion, the temperature and radiation were measured and the actual burning process was recorded by a video camera. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and chemical analysis were performed on the both initial powders and final products. It was found that the powders, ignited by local heating, burned in a two-stage self-propagating regime. The products of the first stage consisted of unreacted aluminum ($\sim 70 \text{ mass } \%$) and amorphous oxides with traces of AlN. After the second stage the AlN content exceeded 50 mass % and the residual Al content decreased to $\sim 10 \text{ mass } \%$. A qualitative discussion is given on the kinetic limitation for AlN oxidation due to rapid condensation and encapsulation of gaseous AlN.

Key words : Superfine aluminum powder, Combustion, Electric explosion of wire oxidizer

1. Introduction

Aluminum powders are widely used as components of propellants and pyrotechnics of various types^{1,2)} and therefore, interest in the combustion mechanism of aluminum powders is increasing³⁾. Although many researchers have reported about the characteristics of the combustion process for micron-sized aluminum particles in numerous oxidizers (burning rate, combustion temperatures, brightness at each stage)^{4,5)}, consistent data have yet to be obtained⁶⁾. The combustion of metal particles is a two or more stage process with the formation and decomposition of tens of products in different gas media¹⁾. Traces of AlN in final products

of combustion were first reported in Ref.⁷⁾. Boborykin et al. proposed a theoretical explanation for the formation of AlN and its subsequent oxidation during combustion of Al in air⁸⁾. Later the role of nitrogen in the combustion of Al was shown to be insignificant⁹⁻¹¹⁾. However, in the work reported here a noticeable role of nitrogen in the combustion of Al in air was found.

Recently superfine metal powders (average particle diameter, a_p : $\sim 0.1 \mu\text{m}$) have drawn much interest as components of propellants¹²⁾. Their thermophysical and chemical properties, however, change drastically as the particle size is decreased substantially. The characteristics of superfine powders are distinguished from those of micron-sized powders mainly through

their lower bulk density ($0.1\text{--}0.3\text{ g/cm}^3$), gas absorption ($3\text{--}5\text{ mass \%}$) and their capillary system¹³. Superfine aluminum powders (SFAP), obtained by the wire electrical explosion (WEE) method¹⁴, are not pyrophoric after slow air-passivation, but can burn in the self-propagating regime in air by local ignition, which makes them different from micron-sized powders¹⁵. The combustion process of a SFAP in air was studied in this work and possible mechanisms for the formation of AlN from gaseous intermediates are discussed.

2. Experimental

SFAP were obtained by the WEE method in an argon atmosphere using facilities developed by the High Voltage Research Institute, Tomsk, Russia (described elsewhere¹⁴). The specific surface area, determined by the BET method, was $10\text{ m}^2/\text{g}$. The aluminum metal content was $C_{\text{Al}}=92\text{ mass \%}$. 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)¹⁶. 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. An optical sensor was employed for measurements of radiation from burning powders. The experiments were carried out in air.

3. Ignition and Combustion

Four grams of superfine aluminum powder were poured onto a steel saucer (see Fig. 1). The shape of the poured powder sample was cone like. For three statistically studied SFAP samples of equal mass (4 g) the ignition temperature determined by pyrometer was $750\pm 100 \div 820\pm 100\text{ K}$. Local ignition was initiated by an electrically heated Ni-Cr alloy wire, which was placed at the top of the cone-like sample. After the ignition, combustion occurs as a non-stationary two-stage process (Fig. 1). In the first stage of combustion: from the ignition point, combustion waves of red color propagated through the surface of the sample (Fig. 1, b-c). The maximal combustion temperature

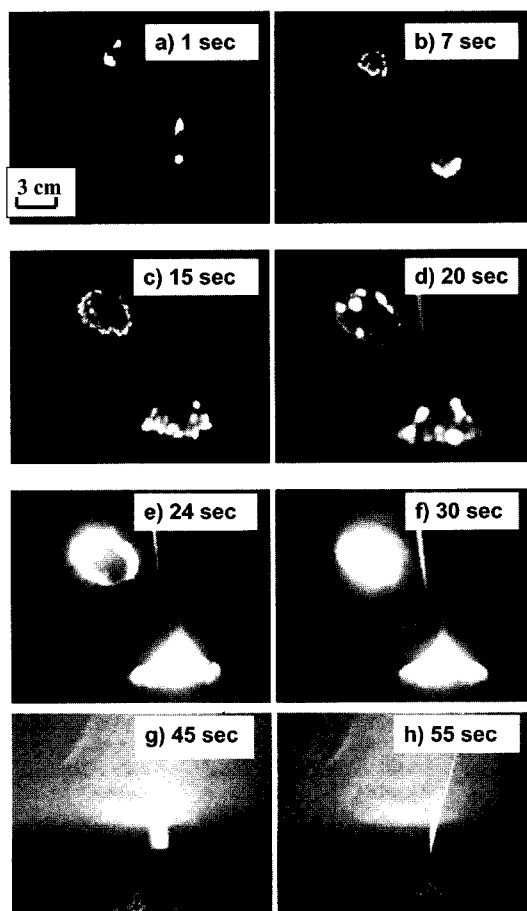


Fig. 1. Video images and reflections of burning of superfine aluminum powders ($m=4\text{ g}$) in air: (a)-(c) the 1st stage, (d)-(f) the 2nd stage, (g)-(h) cooling.

during stage 1 did not exceed $1400\pm 100\text{ K}$ (measured by pyrometer), but temperature increase is not reflected on the temperature curve (Fig. 2) because the thermocouple was placed in the center of the conic sample. After a rather slow first stage a fast and spontaneous temperature increase up to $2500\pm 50 \div 2800\pm 50\text{ K}$ (measured by thermocouple) was observed accompanied by bright radiation of white color (stage 2). The second stage usually began from the center of the sample and then propagated through the whole sample volume (Fig. 1 d-f). After the second stage when the main part of the SFAP was reacted, the sample was cooled down fast (Fig. 1g-h).

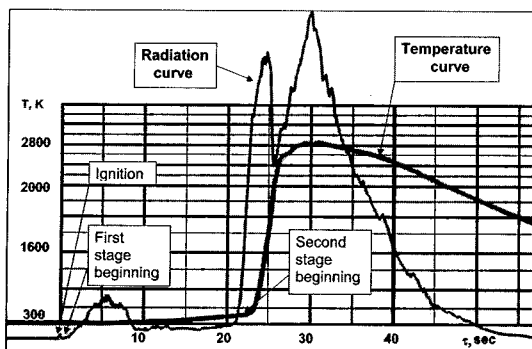


Fig. 2. Radiation and temperature history of superfine aluminum powders ($m=4$ g) burning in air.

4. Composition and Structure of the Combustion Products

XRD and chemical analyses showed that the product of the first stage, which was quenched by a fast placing to argon, consisted of unreacted aluminum and

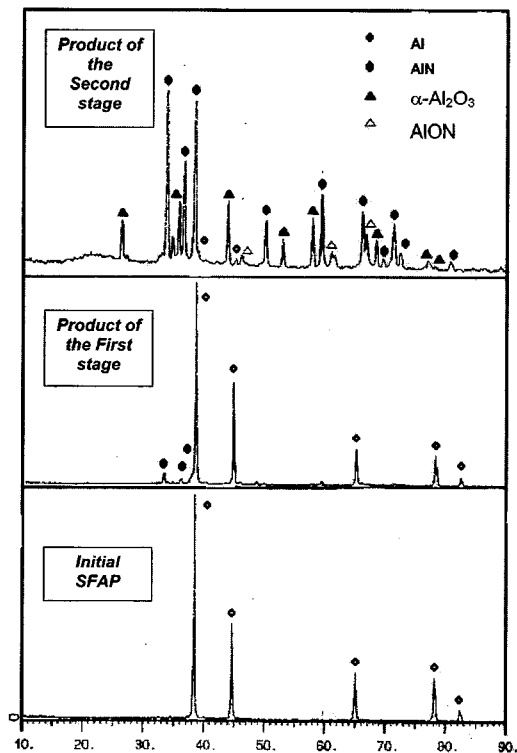
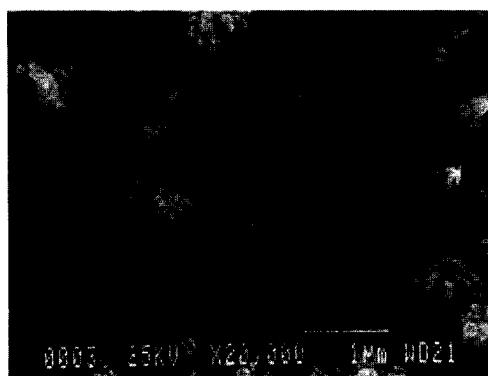


Fig. 3. X-ray diffraction patterns of initial SFAP and products of their combustion in air ($\text{CuK}\alpha$ irradiation, $\lambda=1.54056$ nm).

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, where the most intensive peaks belong to the Al phase. After the second stage of SFAP combustion, the content of aluminum metal in the 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 the air is assumed to be 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 with the final products consisting of needle-like polycrystals of micron and submicron size (Fig. 4 b,c).

5. Results and Discussion

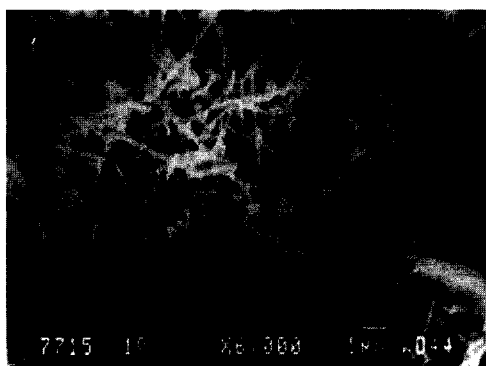
The phenomenon of the formation of a large amount of AlN (50 mass %) by combustion of layer of SFAP in air was first observed in Ref.¹⁷. In that work authors have shown that more than 50 mass % of AlN (AlON) was formed by combustion of a cone-like pile of ultrafine aluminum powder in air. But in that work the process of combustion was only monitored by a thermocouple and therefore the results of that work were semiquantitative. Later, other authors¹⁸ have demonstrated the AlN formation in an experiment on combustion of mechanically activated aluminum and graphite mixtures in air. They activated micron-sized Al+C powders of different ratios (1/7÷7/1) in a ball mill under argon atmosphere. Activated Al+C powders ($m\approx 10$ g) self-ignited immediately after coming into contact with air and then burned in a two-stage regime with the presence of the high-temperature stage. Tsuchida et al.¹⁸ assume that the mechanism of AlN formation includes the reaction of CO_2 formation and Al_3C_4 formation and nitration. The mechanism of AlN formation has not been investigated in detail until now, although in these three cases (present work,^{17,18}) the mechanism of combustion is the same (the burning regimes are similar and a final prime reaction product is AlN). The main question is why nitrogen instead of oxygen reacts with alumi-



(a)



(b)



(c)

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

num. In some AlN synthesis studies AlN intensively reacted with oxygen to form Al_2O_3 if traces of oxygen¹⁹ appeared.

The final products of SFAP combustion in air are formed under conditions of high temperature ~ 2800 K

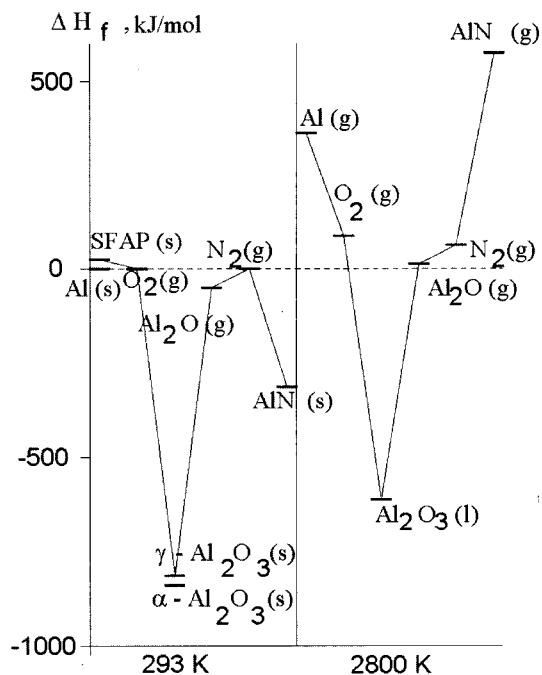
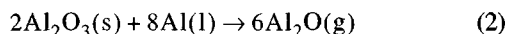
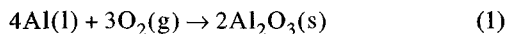


Fig. 5. Thermodynamic diagram of oxidation and nitridation of aluminum under mixed atmosphere of oxygen and nitrogen.

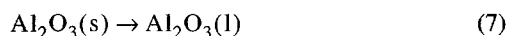
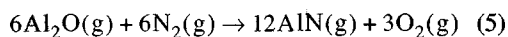
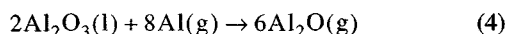
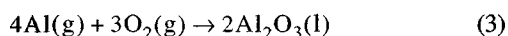
(Fig. 2). In this case the oxidation of aluminum nitride does not occur, which is apparently connected with the encapsulation of nitrides by Al_2O_3 , protecting nitride from oxidation. The initial powders are agglomerates of sphere-like particles, whose average diameter is substantially less than $1 \mu\text{m}$ (Fig. 5a). However, the products of combustion show a skeleton of a spongy structure (Fig. 5b). The structural fragments of this structure are elongated crystals with lengths of tens of micrometers and thicknesses up to $1 \mu\text{m}$ (Fig. 4 b,c). From such structural characteristics of the final product of SFAP combustion - the needle like crystals - it can be assumed that the formation of the final product proceeded with the participation of a gaseous intermediate product²⁰.

The presence of the AlN phase in the final products of SFAP combustion is one of the main features of SFAP combustion, which contradicts to thermodynamic calculations (the nitride must be further oxidized in air). During some period of time the accumulation of AlN might be assumed as 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 occurs only under the encapsulation 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. Such a combustion behavior of metals in gaseous oxidizers is well known for SHS systems²¹. The combustion occurs in "layer by layer" regime and the temperature gradients and the diffusion coefficient for such processes are described elsewhere²¹. According to XRD analysis (Fig. 3), the main phase after the first stage of combustion of the SFAP in air 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 Al_2O_3 . On the other hand, the burning temperature of the samples is lower than 1400 K. Additionally, the volatility of Al_2O_3 increases 2 times by the presence of melted aluminum¹. Hence, we can assume that probable reactions during the first combustion stage are:



After the slow first stage of combustion the sample temperature rapidly increases up to 2800 K, most probably because of the change of combustion to gaseous intermediates oxidation and nitration by the components of air. At high temperatures ($T \approx 2800$ K) it is necessary to consider the reactions:



Thus, we assume that aluminum nitride is formed in the second stage of the combustion process through gaseous suboxides and then encapsulated by Al_2O_3 . The probability of such a way of aluminum nitride formation could be shown by thermodynamic calculations. The diagram of the thermodynamic states of the

initial, intermediate and final products of aluminum combustion in the presence of oxygen and nitrogen is given in Fig. 5. Analysis of the diagram shows that the sole source of heat at a high temperature (2800 K) is the oxidation of aluminum to Al_2O_3 . The formation of $AlN(g)$ at 2800 K is an endothermic process with $\Delta H_f^{2800K}(AlN(g)) \approx 585$ kJ/mole. After the formation of AlN in the gas phase (Fig. 5) condensation occurs for lower temperatures with heat liberation. The temperature consecutively increases during the second stage of combustion of SFAP and decreases (Fig. 2, radiation oscillations on the temperature curve) due to aluminum oxidation (temperature increase) and aluminum nitride formation (temperature decrease). Dreizin recently reported such radiation oscillations during combustion of micron sized aluminum particles in N_2/O_2 gaseous mixtures³. Possibly, the nature of these processes is the similar.

Thus, at low temperatures (Fig. 5) Al_2O_3 , Al_2O and AlN are formed with heat liberation. But at high temperatures only the Al_2O_3 formation is exothermic (see Fig. 5). The formation of AlN in the gas phase can be assumed to be an endothermic reaction (5) at the second (high-temperature) stage of the SFAP combustion (Fig. 5). In this case two alternative effects arise: one is the increase of the combustion rate and temperature and the other is the reduced magnitude of the thermal effect. The liquid phase of AlN under the conditions of this experiment does not exist. Gas condenses into the solid state, while Al_2O_3 is formed from the liquid state. It might be possible to say that the localization of the oxidation process with the formation of aluminum suboxides and high combustion temperature allows the process of nitride formation. If we consider the delocalized combustion of single particles of SFAP or aerosols consisted of superfine aluminum particles in air, probably, AlN will be suboxidized after formation of ones. Thus, for SFAP combustion in air, aluminum does not react with oxygen, 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 formation and stabilization of nitrides during combustion of powdery elements in air is a normal feature not only for aluminum (present article) and boron²² but also for zirconium²³. It was also recently discovered that during the oxidation of

powdered lanthanum in air, the final products contained 50 mass % of LaN²⁴.

Summary

Combustion of superfine aluminum powders in air takes place as a two-stage process.

During the first stage the combustion temperature does not exceed 1400 K. The combustion product mainly consists of unreacted Al and amorphous Al oxides, whereas only small traces of AlN are found. A substantial increase in combustion temperature (up to 2800 K) as well as AlN content is measured after second stage. AlN is presumably formed through gaseous suboxides and subsequently encapsulated by Al₂O₃. Its oxidation is thermodynamically favorable but kinetically hindered due to rapid cooling and condensation.

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References

1. P. F. Pokhil, A. F. Belyaev, Y. V. Frolov, V. S. Logachev and I. A. Korotkov: *Combustion of Powdered Metals in Active Media*. Nauka, Moscow (1972).
2. K. K. Kuo and M. Summerfield: *Fundamentals of Solid Propellant Combustion*, AIAA, New York (1984).
3. E.L. Dreizin: *Combust. Flame*, **117** (1999) 841.
4. J. Servaites, H. Krier, J. C. Melcher and R. L. Burton: *Combust. Flame*, **125** (2001) 1040.
5. Z. Ji, and L. Shufen: *Propellants, Explosives, Pyrotechnics*, **24** (1999) 224.
6. Y. Zhu and Y. Saburo: *Combust. Flame*, **115** (1998) 327.
7. V. M. Gremyachkin, A. G. Istratov and O. I. Leipunskii: *Combust. Explos. Shock Waves*, **11** (1975) 313.
8. V. M. Boborykin, V. M. Gremyachkin, A. G. Istratov, V. I. Kolesnikov-Svinaryov, G. P. Kuznetsov, O. I. Leypunskiy and V. M. Puchkov: *Combust. Explos. Shock Waves*, **19** (1983) 270.
9. E. L. Dreizin: *Combust. Flame*, **105** (1996) 541.
10. S. Yuasa, Y. Zhu and S. Sogo: *Combust. Flame*, **108** (1997) 387.
11. M. T. Swihart and L. Catoire: *Combust. Flame*, **121** (2000) 210.
12. M. M. Mench and K. K. Kuo, C. L. Yeh, Y. C. Lu: *Combust. Sci. Tech.*, **135** (1998) 269.
13. A. P. Ilin and A. A. Gromov: *Oxidation of Aluminum and Boron Superfine Powders* (in Russian). Tomsk Polytechnic University, Tomsk (1999).
14. Y. S. Kwon, Y. H. Jung, N. A. Yavorovsky, A. P. Ilyin and J. S. Kim: *Scripta mater.*, **44** (2001) 2247.
15. A. P. Ilin, A. A. Gromov, V. I. Vereshchagin, E. M. Popenko, V. A. Surgin and H. Lehn: *Combust. Explos. Shock Waves*, **37** (2001) 664.
16. T. D. Fedotova, O. G. Glotov and V. E. Zarko: *Propellants, Explosives, Pyrotechnics*, **25** (2000) 325.
17. A. P. Ilin and L. T. Proskurovskaya: *Combust. Explos. Shock Waves*, **26** (1990) 190.
18. T. Tsushida, T. Hasegawa and M. J. Inagaki: *Amer. Ceram. Soc.*, **77** (1994) 3227.
19. F. J. - M. Haussone: *Materials and Manufacturing Processes*, **10** (1995) 717.
20. A. P. Ilin, A.P., A. A. Gromov, G. V. Yablunovskii, E. M. Popenko and N. V. Bychin: *Combust. Explos. Shock Waves*, **35** (1999) 656.
21. A. G. Merzhanov: *Journal of Mater. Process. Technol.*, **56** (1996) 222.
22. A. P. Ilin, A. A. Gromov, V. I. Vereshchagin: *V-th Russian-Chinese International Symposium "ADVANCED MATERIALS AND PROCESSES" / Fundamental Problems of Developing Advanced Materials and Processes of the XXI Century/ (AMP99)*, July 27th - August 1st 1999, Baikalsk, Russia, (1999) 217.
23. A. P. Ilin, V. V. An, V. I. Vereshchagin and G. V. Yablunovskii: *Combust. Explos. Shock Waves*, **36** (2000) 209.
24. V. G. Shevchenko, V. I. Kononenko, I. A. Chupova, I. N. Latosh, N. V. Lukin: *Combust. Explos. Shock Waves*, **35** (1999) 79.