Combustion, Explosion, and Shock Waves, Vol. 38, No. 1, pp. 123–126, 2002

URGENT COMMUNICATION

Properties of Ultrafine Aluminum Powder Stabilized by Aluminum Diboride

A. P. Il'in,[1] A. A. Gromov,[1] D. V. Tikhonov,[1] G. V. Yablunovskii,[1] and M. A. Il'in[1]

UDC 541.16:182

Translated from *Fizika Goreniya i Vzryva*, Vol. 38, No. 1, pp. 139–142, January–February, 2002.
Original article submitted;August 21, 2001.

The paper studies properties of an ultrafine aluminum powder produced by electric explosions of conductors, whose particles are stabilized by coating with aluminum diboride immediately during the synthesis of the powder. The ultrafine aluminum powder stabilized in such a manner has special properties: narrow particle size distribution, increased dispersity, and higher resistance to oxidation upon heating.

INTRODUCTION

It is well known that the substitution of ultrafine powders (UFP) for coarsely dispersed aluminum powders (10–100 μm) in propellants increases the completeness of aluminum combustion, decreases the agglomeration of combustion products, and reduces two-phase losses [1, 2]. With increase in the dispersity of aluminum, and, hence, its reactive surface area, the propellant burning rate increases significantly. At present, ultrafine aluminum powders (UFAP) produced by electric explosion of conductors have been studied most extensively [3–9], and interest in this UFP is still growing [10]. An electric explosion of conductors (power density $> 10^{13}$ W/cm^3 and process duration 1–10 μsec) can lead to stabilization of metastable structures, which relax at relatively low temperatures, thereby enhancing the reactivity of the UFP produced by electric explosion [11]. As a rule, an increase in dispersity of UFP increases the reactivity of these powders, simultaneously reducing the metallic aluminum content [4, 5]. Another problem of the ultrafine state is the agglomeration of UFP, which is associated with reactive particle surfaces. The presence of agglomerates of particles leads to nonuniformity of the mixtures and sintering of the agglomerates in the heating zone during combustion. As a result, the formation of large drops obliterates the advantages of UFP.

It has been established experimentally that the addition of chemically active gases (O_2 and N_2) to argon increases dispersity of products of electric explosion of conductors [3]. In this case, a decrease in the characteristic particle size is due to a decrease in the contribution of agglomeration and sintering into the formation of products of electric explosion of conductors. The presence of heat-resistant nonmetallic compositions reduces agglomeration during heating of UFP in the same manner as during combustion of aluminum particles encapsulated by more heat-resistant metals [12]. In addition, this simplifies passivation of UFP that are coated with an oxide or nitride layer. The stabilization of UFAP due to formation of an oxide film leads to a loss of 3–6% of the aluminum mass and to a decrease in the energy content of the powder. In the case of addition of nitrogen, the aluminum nitride produced by electric explosion is oxidized during passivation and hydrolyses. Therefore, aluminum oxide (hydroxide) is a protective film in this case, too.

Thus, to improve the properties and characteristics of UFAP, it is necessary to use a novel approach to this problem. As an alternative to oxide and nitride protective films, Il'in et al. [13] proposed a protective coating of aluminum boride applied to aluminum particles during electric explosion. In contrast to inert aluminum

[1]High-Voltage Institute at the Tomsk Polytechnic University, Tomsk 634050; yellow@mail2000.ru.

0010-5082/02/3801-0123 $27.00

TABLE 1

Properties of Aluminum Powders Produced by Electric Explosion

Sample No.	Medium of electric explosion	W/W_{sub}, rel. units	S_{sp}, m^2/g	$[Al^0]$,* %	$[Al_2O_3]$, % (calculation)	Notes
1	Ar	1.38	17.0	78.0 + 18.0% $[AlB_2]$	>1.0	—
2	Ar	1.45	9.3	88.5	5.5	—
3	$Ar + N_2$	1.64	16.0	89.0	5.0	—
4	Ar	2.15**	12.1	94.8	4.0	According to [15]

Notes. The specific surface area of the samples (S_{sp}) is determined by the BET (Brunauer–Emmett–Teller) method. $[Al^0]$ is the mass concentration of the unoxidized metal; one asterisk indicates that adsorbed and absorbed gases contained in UFP are not taken into account. Two asterisks indicate that the value calculated by available correlation dependences [4].

oxide, the heat released during combustion of, for example, aluminum diboride reaches 2025.5 kJ/mole.

EXPERIMENT AND DISCUSSION

According to x-ray photoelectron spectroscopy data (ESCALAB-5 spectrometer), the UFAP particles produced by explosion of an aluminum conductor coated with boron are encapsulated with a boride film whose composition is close to AlB_2. According to x-ray phase analysis (DRON-3M diffractometer and CuK_α radiation), the UFAP consists of the aluminum phase; the aluminum diboride phase was not detected, probably, because it is amorphous to x-rays. In the photograph of such UFAP (JSM-840 scanning electron microscope), it is seen that the particle diameters differ only slightly from each other. Generally, the particle diameter is less than 100 nm. The explosive production of powders with a narrower particle size distribution is possible by increasing the energy supplied to the conductor and using reactive gases [3] or reagents. Table 1 lists characteristics of UFAP coated with aluminum boride (sample No. 1) and other explosively produced aluminum powders (sample Nos. 2–4).

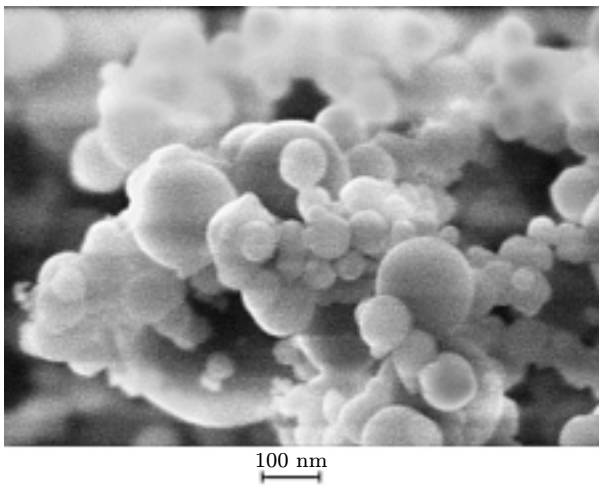

Fig. 1. Photograph of UFAP coated with aluminum boride.

When the primary products of an electric explosion ($T \sim 10^4$ K) are cooled to the temperature below the upper temperature limit for chemical reactions ($T \sim 5 \cdot 10^3$ K), heat-resistant compounds are formed, which diminish agglomeration and sintering of particles. The presence of boron (see sample No. 1 in Table 1) or the addition of nitrogen to argon (sample No. 3) during electric explosion results in a twofold increase in the specific surface of such UFAP compared to the UFAP produced in argon (sample No. 2). For sample Nos. 1–3, the specific electric energy [W/W_{sub}, where W_{sub} is the heat (energy) of sublimation of the conductor] supplied to the conductor decreased insignificantly, i.e., in the presence of additives, the energy expended in the formation of 1 m^2 of the surface also decreases by a factor of about two (see Table 1).

The reactivity of the examined UFAP samples was analyzed for the parameters proposed in [14], which were obtained using differential thermal analysis (DTA) under standard conditions. The reactivity of UFAP was determined using four parameters: the temperature of the onset of oxidation (T_{in} [°C]), the maximum oxidation rate (v_{ox} [mg/min]), the degree of conversion (the degree of oxidation) of aluminum in a specified temperature range (α [%]), and the reduced (conditional) thermal effect ($S/\Delta m$ [rel. units]), which is determined as the ratio of the area of the peak of heat release (DTA curve) to the weight increment of the examined sample. The standard weight of the UFAP samples was $\approx 5 \cdot 10^{-5}$ kg and the heating rate was $\approx$10°C/min. Table 2 shows the reactivity parameters of the exam-

TABLE 2

Parameters of the Reactivity of Aluminum Powders Produced by Electric Explosion

Sample No.	T_{in}, °C	α,%		v_{ox}, mg/min (T, °C)	$S/\Delta m$, rel. units	ΔH^{298}_{burn}, kJ/g (calculation)	Notes
		up to 660°C	up to 1000°C				
1	580	34.0	77.8	3.2 (580–600)	6.3	31.6	—
2	540	40.0	70.0	5.6 (545–570)	5.6	27.5	—
3	540	49.7	78.5	3.0 (550–605)	8.7	27.6	—
4	550	39.4	45.0	3.0 (541–555)	—	29.4	According to [15]

ined UFAP samples and the "Alex" powder ("Argonide Corp.").

According to the data shown in Table 2, coating of the particles with aluminum diboride increases the resistance of UFAP to heating: the temperature of the onset of oxidation is 30–40°C higher for boride-coated aluminum powders than for powders with oxide–hydroxide coating. Upon heating to 660°C, the degree of oxidation of sample No. 1 is ≈6–16% lower than that of sample Nos. 2–4, whose oxidation starts at lower temperatures. Upon heating to 1000°C, most of the UFAP (70–78.5%) is oxidized; only particles of micron sizes or large drops formed during coalescence and sintering of the UFAP particles remain. Upon heating to 1000°C, less than half (45%) of sample No. 4 is oxidized: its oxidation at a temperature higher than 1000°C proceeds similarly to the oxidation of commercial ASD-4 powder [5, 9].

The maximum values of v_{ox} for sample Nos. 1, 3, and 4 differ slightly from each other. However, the maximum value of v_{ox} corresponds to sample No. 2 with the lowest dispersity: the higher rate can be associated with relaxation processes. There is an inverse relationship between the maximum oxidation rate and the heat effect determined experimentally ($S/\Delta m$). This can be due to increased heat losses at higher oxidation rates (see Table 2). The calculated heats of combustion of the examined samples show that the additional heat (2–4 kJ/g) is released when the oxide-hydroxide film on the particles is replaced by an AlB_2 coating.

Thus, an aluminum diboride coating applied to the surface of UFP particles during electric explosion of aluminum conductors results in a nearly twofold increase in dispersity due to a decrease in agglomeration. In this case, the properties of UFP particles coated with boride change: the heat resistance of such particles becomes higher (by 30–40°C) than that of the UFP produced in argon or argon–nitrogen media. More than 40% of the aluminum contained in the UFP whose particles are coated with aluminum diboride is oxidized in the temperature range of 660–1000°C. According to the calculation results, replacement of the oxide-hydroxide protective coating by an aluminum diboride coating increases the heat of combustion of UFP by 2–4 kJ/g.

This work was supported by the Russian Foundation for Fundamental Research (Grant No. 01-02-17948).

REFERENCES

1. P. F. Pokhil, A. F. Belyaev, Yu. V. Frolov, V. S. Logachev, and A. I. Korotkov, *Combustion of Metal Powders in Reactive Media* [in Russian], Nauka, Moscow (1972).
2. F. Tepper, G. Ivanov, M. Lerner, and V. Davidovich, "Energetic formulations from nanosize metal powders," in: *Proc. Int. Pyrotech. Seminars*, No. 24, Chicago (1998), pp. 519–530.
3. M. I. Lerner, "Control of the formation of superfine particles under conditions of electric explosions of conductors," Candidate's Dissertation in Tech. Sci., Tomsk (1988).
4. A. P. Lyashko, "Structure of submicron aluminum powders and their interaction with water," Candidate's Dissertation in Chem. Sci., Tomsk (1988).
5. L. T. Proskurovskaya, "Physicochemical properties of ultrafine aluminum powders produced by electric explosion," Candidate's Dissertation in Chem. Sci., Tomsk (1992).
6. O. B. Nazarenko, "Formation of products from electric explosion of conductors in condensed media," Candidate's Dissertation in Tech. Sci., Tomsk (1996).
7. V. V. An, "Use of nanosize aluminum powders in the production of nitride-containing materials," Candidate's Dissertation in Tech. Sci., Tomsk (1999).
8. D. V. Tikhonov, "Production of ultradisperse powders of complex composition by electric explosion," Candidate's Dissertation in Tech. Sci., Tomsk (2000).
9. A. A. Gromov, "Production of nitride-containing materials during combustion of ultrafine powders of aluminum and boron," Candidate's Dissertation in Tech. Sci., Tomsk (2000).
10. *Physical Chemistry of Ultradisperse Systems*: Proc. V All-Union Conf. (Oct. 9–13, 2000), Izd. Mosk. Inzh.-Fiz. Inst., Moscow (2000).

11. A. P. Il'in, "On the excessive energy of ultradisperse powders produced by explosions of conductors," *Phys. Khim. Obr. Mater.* (collected scientific papers), No. 3 (1994), pp. 94–97.
12. A. L. Breiter, V. M. Mal'tsev, and E. I. Popov "Means of modifying metallic fuels in condensed systems," *Fiz. Goreniya Vzryva*, **26**, No. 1, 97–104 (1990).
13. A. P. Il'in, Yu. A. Krasnyatov, and D. V. Tikhonov, "Method of producing powders," Patent of the Russian Federation, No. 2139776.
14. A. P. Il'in, G. V. Yablunovskii, and A. A. Gromov, "Reactivity of aluminum powders," *Fiz. Goreniya Vzryva*, **37**, No. 4., 58–62 (2001).
15. M. M. Mench, K. K. Kuo, C. L. Yeh, and Y. C. Lu, "Comparison of thermal behaviour of regular and ultrafine aluminum powders (Alex) made from plasma explosion process," *Combust. Sci. Technol.*, **135**, 269–292 (1998).