



Study of Non-isothermal Nitridation of Aluminum Nanopowders Passivated by Non-oxide Layers^{*)}

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Abstract: Results of DTA-TG investigation and chemical analysis of electro-exploded aluminum nanopowders coated and/or passivated with the reactive reagents: nitrocellulose (NC), oleic ($C_{17}H_{33}COOH$) and stearic ($C_{17}H_{35}COOH$) acids, amorphous boron and air (for a comparison) are discussed. Surface protection of aluminum nanopowders by coatings of different origin results in significant advantages in the energetic properties of the powders. Aluminum nanopowders with a protecting surface show increased stability to oxidation during storage period.

Keywords: aluminum nanopowder, surface passivation, energetic properties, DTA-TG

Introduction

Nowadays a number of new synthesized energetic materials have been reported and generated much discussion. One of the most interesting newly developed material is aluminum nanopowder (ANP) used as a propellant booster [1]. This material can be produced by several methods, but the highest

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productivity of them ($\sim 150 \text{ g h}^{-1}$ for one facility unit) is the electrical explosion of wires (EEW). This method is characterized by a high rate of energy input into the material. Electro-exploded ANPs after stabilization and air-passivation contain 80-85 wt.% of metallic aluminium and are protected from further oxidation by an Al_2O_3 film. But, 20-25 wt.% of “oxide ballast” in ANPs leads to the loss of a number of advantages for their use in propellants in comparison to micron-sized powders which have a content of metallic aluminium up to 99.5 wt.%. Moreover, the 42-70 wt.% of active Al for particles of 60 nm in diameter was found in the recent studies of ANP reactions in energetic mixtures with NC [2]. Thus, studies how to increase the metal content of EEW-ANPs should be concentrated in two directions: search for appropriate passivating and coating reagents for nanopowders to reduce the oxide formation during production and simultaneously to increase the stability of ANPs towards oxidation during storage and mixing with propellant binders (HTPB, GAP etc.).

This specific motivation attracts powders which are coated by reactive reagents directly during ANP production (explosion in Ar) or after particles' formation and cooling before contact with air [3], because the surface of Al particles immediately oxidizes when contacted with air. All after-oxidation-treatment cannot remove such oxide layers from the particle surface. Hence, we cannot store more metal in the particle.

The results of DTA-TG investigation in nitrogen of electro-exploded ANPs coated and/or passivated with the non-oxide reagents: nitrocellulose (NC), oleic ($\text{C}_{17}\text{H}_{33}\text{COOH}$) and stearic ($\text{C}_{17}\text{H}_{35}\text{COOH}$) acids, amorphous boron and air (for the comparison) are given in this work. Nitrogen as a media for DTA-TG study has been selected for 2 reasons: it is one of the components of a flame for modern fast-burning propellants and nitrogen-containing compounds (ADN, HMX, TNT etc.) come into contact with ANPs during propellant fabrication and storage.

Experimental Results and Discussion

Aluminum nanopowders' preparation and passivation

Parameters for powder production are shown in Table 1. Production of the ANP samples was carried out by using an EEW machine of the 4th generation UDP-4G which was constructed for the mass production of metallic nanopowders at the High Voltage Research Institute, Tomsk Polytechnic University, Russia. The characteristics of the UDP-4G machine are comprehensively described elsewhere [4].

Table 1. Parameters of production for electro-exploded aluminum nanopowders

Nanopowder	Voltage by EEW [kV]	Energy input [a.u.]	Capacitance [μ F]	Inductivity [μ H]	Resistance [Ω]	Wire diameter [mm]	Wire length [mm]	Ar pressure [MPa]
Aluminum	26	1.4	2.17	0.6	0.07	0.35	70	0.15

Non-passivated ANPs immediately self-ignite if exposed to air, making passivation essential. Hence, after the EEW machine stopped, the collector with prepared powder was placed into a separate hermetic passivation chamber immediately after powder production. Four samples, studied within this work and their specific surface area, determined by BET method, as well as metal aluminum content (C_{Al}), measured by volumetric analysis, and volume mean particle diameter (a_v) are shown in Table 2.

Table 2. Properties of aluminum nanopowders

No	Sample code	Initial wire composition	Gas media in explosive chamber	Passivation condition	BET [m ² /g]	a_s^* [nm]	a_v^{**} [nm]	C_{Al} [wt.%]
1	Al (Air)	Al	Ar	Air	18.6	119	553	85
2	Al (B)	Al (B)	Ar	Air	12.0	185	610	84
3	Al (St Ac)	Al	Ar	Stearic acid in ethanol	12.1	184	255	74
4	Al (Ol Ac)	Al	Ar	Oleic acid in ethanol	14.3	155	393	45
5	Al (NC)	Al	Ar	Nitrocellulose in ethanol	12.6	176	-	68

* Calculated surface mean particle diameter, $a_s = 6/(BET \cdot 2.7)$.

** Measured volume mean particle diameter ("Zetasizer 3000" by Malvern Instruments Ltd., UK).

Sample 1 – ALEX™ analogue – was produced at the High Voltage Research Institute by the UDP-4G machine. Sample 2 was obtained from the composite Al-B wire. Air-passivation was carried out at the room temperature in the medium of argon gas (pressure of 1.1 atm) having an air content of about 0.1 vol.%. These conditions of air-passivation for metal nanopowders were discussed in a previous paper [2]. ANP samples 1-2, Table 2, were completely passivated by an Ar+0.1 vol.% air mixture for 72 hours. The end of the passivation period

was determined as the moment when the nanopowder stopped reacting with air, i.e. when the pressure of the gas mixture in the passivation chamber stopped decreasing. Samples 3-5 were passivated by organic substances in solvents:

- 0.1 wt.% stearic acid, $C_{18}H_{36}O_2$ solution in ethanol (C_2H_6O);
- 0.1 wt.% oleic acid, $C_{18}H_{34}O_2$ solution in ethanol (C_2H_6O);
- 0.1 wt.% nitrocellulose solution in ethanol (C_2H_6O).

The solution for passivation was added to the fresh powder immediately after production and the powder solution was mechanically stirred for ~2 hours. The temperature was kept lower than 30 °C in order to avoid self-heating and partial self-sintering of the powder. All powders were stored in open-to-atmosphere boxes for 2 months after passivation to simulate conditions, close to industrial.

Reduction in the specific surface area (BET) of samples 2-5, passivated by non-oxide layers, can be caused by the residue of solvent on the particles compared to sample 1 passivated by air. This is confirmed by a reduction of the content of Al metal (C_{Al}) in samples 2-5: the reduction is maximal for ANP passivated by oleic acid – down to 45 wt.%. Hence, coating of particles by organic reagents leads to considerable reduction of the specific metal content in the powder.

Aluminum nanopowders characterization

DTA-DSC-TG (STA 409 C, Germany) was used for the study of the reactivity of ANPs in N_2 . TEM-EDX study provided by the University of Karlsruhe (apparatus Philips (FEI) CM 200 FEG, electron source – field emitter (Shottky-type), 200 kV). SEM-EDX investigations were performed with the “JSM-6500 F” (JEOL, Japan) apparatus, which includes a field emission gun. XRD analyses were carried out using a “MAX-B” diffractometer (Rigaku, Japan) with CuK_{α} radiation (Ni-monochromated). The “Zetasizer 3000” by Malvern Instruments Ltd., UK, was used for the determination of the particle size.

The results of the TEM-EDX and XRD study of ANPs are presented in Table 3. All powders contain more than 10 wt.% of oxygen (as Al_xO_y) on the particle surface. Traces of aluminum carbide were found by XRD for samples 3 and 4 (carbon) was not determined by EDX.

Table 3. Elemental and phase composition of aluminum nanopowders

No.	Sample code	Wt. content of elements, % (EDX)		Phase composition (XRD)
		O	Al	
1	Al (Air)	15.5	84.5	Al
2	Al (B)	10.9	89.1	
3	Al (St Ac)	15.1	84.9	
4	Al (Ol Ac)	18.3	81.7	Al, traces of Al ₄ C ₃
5	Al (NC)	n/a		

According to TEM observation, the concentration of Al inside the particles increases by application of organic coatings (Figure 1), while the specific metal content C_{Al} is lower for powders passivated by organic substances (Table 2). It should be noted that the term “specific metal content” characterizes the content of metal in the powder, but not in the particle. The content of metal in ANP, passivated by oleic acid, can be higher than for ANP, passivated by air (Figure 1a). According to TEM data, particles, passivated by air, are covered with an oxide film (thickness of 4-5 nm), while particles, passivated by oleic acid (Figure 1b) do not have an oxide layer. Analyzing Figure 1a, we can observe the beginning of oxide film crystallization, i.e. the critical thickness for amorphous oxide film is 7-8 nm, after that crystallization begins. According to SEM results, on the contrary, organic-passivated particles hold on their surface a lot of residual solvents (Figure 2): particles are not separated as in the case of “dry” powders.

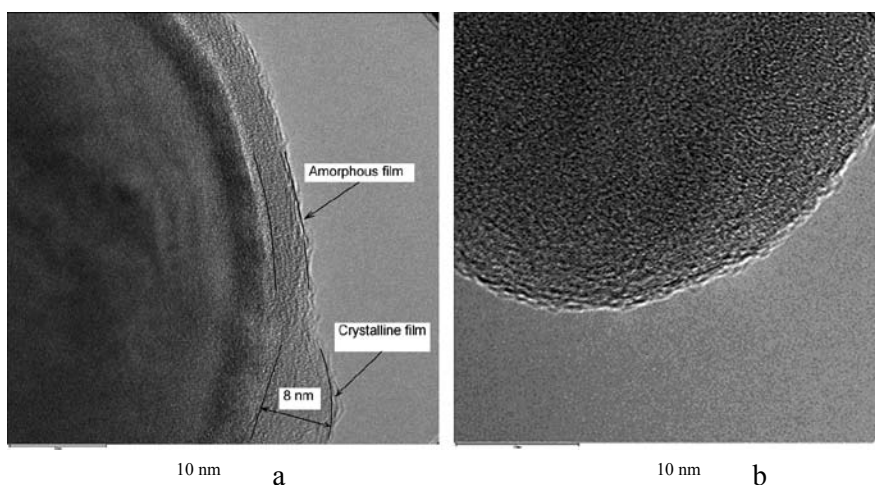


Figure 1. TEM images of ANPs passivated by air (a, sample 1) and oleic acid (b, sample 4).

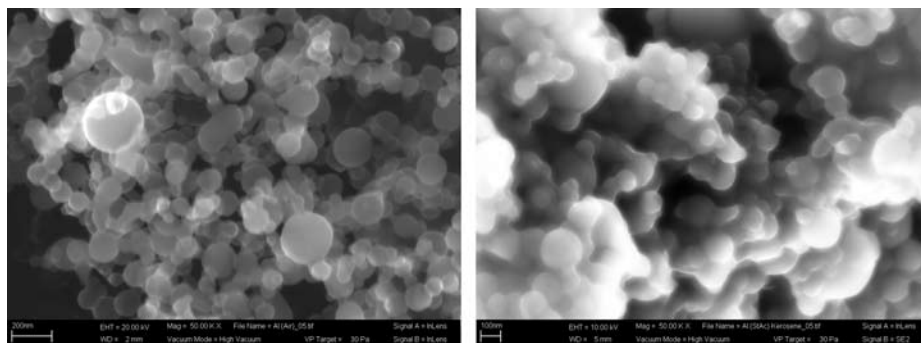


Figure 2. SEM images of ANPs passivated by air (a, sample 1) and stearic acid (b, sample 3).

Aluminum nanopowders' non-isothermal nitridation

Results of the indirect estimation of the content of metallic aluminum in ANPs according to the heat of melting ($\Delta H_{melt} Al$, Table 4) show that the highest metal content possesses the powder, whose particles are covered by boron (see also C_{Al} , Table 1). The minimum temperature of the beginning of nitridation had ANP (NC) (sample 5, Table 4), which, probably, is caused by the preliminary activation of its surface during NC decomposition ($T_{dec}=195\text{ }^{\circ}\text{C}$, Figure 3). The most stable to nitridation (highest T_{nitrid}) is sample ANP (Air), which, probably, is explained by the large strength of fresh amorphous oxide films on the particles. The exothermic effect of nitridation ($\Delta H_{nitrid} Al$) is maximal for the sample ANP (Air). Sample ANP (NC) also had the high heat of nitridation (3940 J g^{-1}), which can be caused by both the simultaneous nitridation of aluminum with decomposition by residual NC and by nitridation of aluminum due to the preliminary activation of the surface. The degree of transformation of Al to AlN (α), was maximum for ANP passivated by oleic acid (sample 4, Table 4). It should be noted that the mass of coating on the particles in the case of NC, stearic and oleic acids is high, which reduces the specific metal content in the powders.

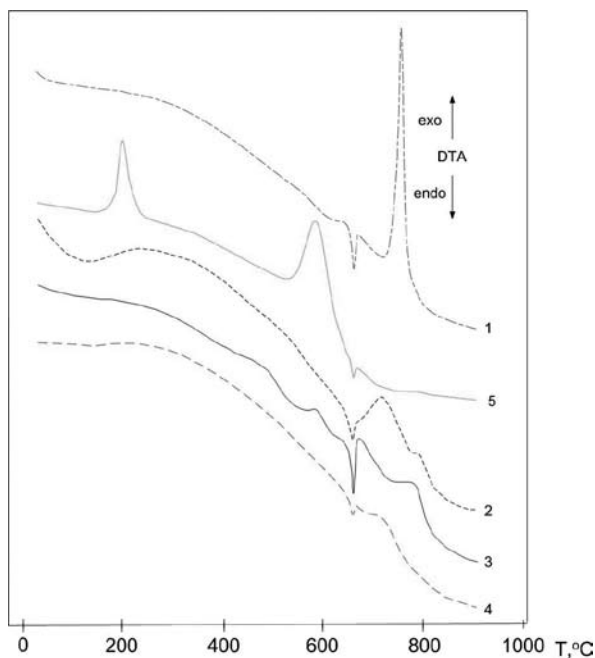


Figure 3. DTA curves for ANPs under non-isothermal heating in nitrogen ($m = 4.4$ mg, $v_{\text{heat}} = 10$ K min^{-1} , etalon α - Al_2O_3). Signs of samples relate to Table 1.

Table 4. Reactivity parameters of aluminum nanoparticles ($m = 4.4$ mg) by non-isothermal heating in nitrogen

No.	Sample code	$\Delta H_{\text{melt Al}}$ (at 660 °C) [J g ⁻¹]	$T_{\text{nitrid onset}}$ [°C]	$\Delta H_{\text{nitrid Al}}$ [J g ⁻¹]	Weight of coating (gases) [%]	α^{***} (500-1000 °C) [%]
1	Al (Air)	-280	798	4270	0.4	76.0
2	Al (B)	-287	749	534	3.3	72.9
3	Al (StAc)	-109	690	584	11.0	37.9
4	Al (Ol Ac)	-84	700	230	11.6	86.0**
5	Al (NC)	-89	553	3940	24.0*	79.3

* Desorption of coating accompanies exo-peak on DTA curve (NC burning for sample 5).

** Up to 900 °C.

*** Degree of conversion α (Al \rightarrow AlN) assuming metal content in the powders (Table 1).

Conclusion

Experimental studies of ANPs passivated by organic and inorganic compositions have been carried out. The applied coatings provide the reaction of metallic particles with nitrogen at lower temperatures. In the case of NC and oleic acid, the degree of transformation of Al to AlN (α) is higher than for air-passivated ANP. Oleic and stearic acid passivation of ANPs results in carbonization of the particles' surface (traces of Al₄C₃ fixed by XRD). The best characteristics under reaction with N₂ show ANPs with NC, air and boron coatings. Hence, their study in aluminized propellants is most promising in future experiments. Passivation of ANPs by non-oxide coatings results in an increase of the metal content inside the particles and, hence, in an increasing of the powder burning enthalpy.

Acknowledgement

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