Non-isothermal oxidation of aluminum nanopowder coated by hydrocarbons and fluorohydrocarbons

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ABSTRACT

Aluminum nanopowder (nAl) obtained by electrical explosion of wires and passivated/coated with hydrocarbons and fluorohydrocarbons is comprehensively characterized. Coatings of different natures (octadecanoic and hexadecanoic acid, (1,1,11) trihydroperfluoro-undecan-1-ol, Fluorel[TM] + ester from esterification of (1,1,11) trihydroperfluoro-undecan-1-ol with furan-2,5-dione) were applied on the particle surface. The powders were studied by TEM, SEM, DSC-TGA, and BET specific surface area. The active aluminum content was determined by volumetric analyses. Coated nAl particles were compared to non-coated powder by the corresponding reactivity parameters obtained from DSC-TGA. It was found that while fatty acids have a weak effect on the non-isothermal oxidation behavior, fluoroelastomers shift the oxidation onset of nAl to higher temperatures by ∼20 °C for the first oxidation stage and by ∼100 °C for the second oxidation stage.

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1. Introduction

The usage of Al nanopowder (nAl) is basically connected with the improvement of energetic systems performance [1,2], the promotion of sintering processes for oxide ceramics [3], the production of aluminum hydroxide fibers by hydrolysis [4], the provision of hydrogen sources for hydrogen energetics [5], and the synthesis of nitride ceramics [6].

Aluminum has a high combustion enthalpy and it is mostly used in energetic systems (propellants, pyrotechnics, explosives and combustion synthesis) [2]. Energetic systems loaded with nAl have faster burning rate and provide more complete burning degree compared to micron-sized Al [7]. The scientific literature about the combustion of nAl loaded solid propellants and solid fuels is extended [1,2,7–9]. Nowadays nAl is a promising new ingredient in the above mentioned areas and interest in it keeps on growing [10].

The passivation layer on the surface of Al nanoparticles determines their reactivity, stability, ignition delay, etc. [11–15]. Some of the recent papers on nAl describe the properties of several particles,

but they are far from large-scale implementation [16]. Large-scale production of nAl is possible by the electrical explosion of wires (EEW) technology [17]. This method is characterized by a process duration of 1–5 μs, plasma temperature ∼10^4 °C, average cooling rate of particles up to 10^9 °C/s and specific energy entering the wire >1 MJ/kg [7,17]. However, a full theoretical explanation of the processes of stabilization and aging of coated metal nanoparticles is still missing [18,19].

Particles of nAl without any protective layers tend to oxidize significantly (at worst to self-ignite) due to chemical reactions triggered by contact with air and atmospheric moisture [15]. For this reason, the surface of industrial nAl is normally passivated by a controlled slow stream of dry gas (Ar + 0.1 vol.% air) for ALEX[TM] or by stearic acid for L-ALEX[TM] [11–14]. In addition to passivation, particles can further be coated by different protective reagents to improve aging characteristics of powders, thus maintaining high metal content and increasing energy release during combustion [12,16]. Application of selected organic layers on particles can also provide better mechanical properties for the polymer matrix including nAl [20].

Application of hydrocarbon and fluorohydrocarbon coating over preliminarily passivated metal particles is a less hazardous process than passivation only [21] and it is expected to provide easier interaction between coating and polymer binder [22]. An experimental investigation of the slow non-isothermal oxidation of passivated

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Nomenclature

α_{1000}	degree of transformation up to 1000 °C (%)
a_s	mean surface particle diameter (nm)
ALEX[TM]	aluminum exploded
C_{Al}	Al metal (or active Al) content (% mass)
ΔH_{ox}	heat release during oxidation [J/g]
Δm_1	initial mass loss in TGA traces (% initial mass)
Δm_{tot}	total mass gain in TGA traces (% initial mass)
DSC	differential scanning calorimetry
EEW	electrical explosion of wires
Fluorel[TM]	fluoroelastomer: vinylidenefluoride hexafluoro-propylene (70:30)
L-ALEX[TM]	stearic acid passivated *nAl*
nAl	aluminum nanopowder
SEM	scanning electron microscopy
S_{sp}	specific surface area (m²/g)
T_{onset}	oxidation onset temperature (°C)
$T_{ox\ peak}$	oxidation peak temperature (°C)
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
UDP-5	machine used for metal nanopowders production by EEW method
XRD	X-ray diffraction

Chemical nomenclature (IUPAC and common names)

Formula	IUPAC/common name
$C_{18}H_{36}O_2$	octadecanoic acid/stearic acid
$C_{16}H_{32}O_2$	hexadecanoic acid/palmitic acid
$H(CF_2CF_2)_5CH_2OH$	(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11) eicosafluoro-undecan-1-ol or (1,1,11) trihydroperfluoro-undecan-1-ol/FTOH 10:1 telomer alcohol
$C_4H_2O_3$	furan-2,5-dione/maleic anhydride

Fig. 1. UDP-5 machine for *nAl* production with the electrical explosion of wires technology: 1 – explosion chamber; 2 – powder deposition system; 3 – powder collector scheme (not installed); 4 – high voltage unit.

and coated *nAl* by DSC-TGA analysis (heating rate 10 °C/min) is discussed in this paper to compare the thermal behavior of coated and non-coated powders. Characterization of *nAl* by SEM/TEM, BET specific surface area, and volumetric analyses was carried out.

2. Experimental

2.1. nAl production

Samples of *nAl* were provided by "Advanced Powder Technology LLC" (Russia). The experimental set-up for *nAl* production is presented in Fig. 1. This production unit represents the next generation (UDP-5) of the machine UDP-4, whose characteristics are reported elsewhere [7,11,17]. The design of UDP-5 aims at reducing the clustering/sintering of particles produced by EEW [23]. This is done by the new implementations of exploded particle extraction path and collector improving the exploded flow gas dynamics and single particle interaction between successive wire explosions. The electrical parameters of the UDP-5 remain the same as for UDP-4. The *nAl* productivity of the UDP-5 set-up is ∼100 g h^{-1}. The relevant production parameters and overall nomenclature are reported in Table 1 and were chosen according to the EEW technology requirements [7].

2.2. nAl passivation, coating and characterization

The *nAl* produced by EEW technique was passivated by two different techniques. In the first one, particles are exposed to a dry atmosphere (Ar + 0.1 vol.% air). In the other, *nAl* is immersed in a proper stearic acid solution immediately after production.

The passivation procedure is described in detail in Ref. [11]. Two batches (100 and 50 nm) of dry air passivated *nAl* were then treated by preliminarily prepared solutions of hydrocarbons and fluorohydrocarbons: octadecanoic acid, hexadecanoic acid, 1H,1H-perfluoroundecan-1-ol (10:1 fluorotelomer alcohol), Fluorel[TM] [24] plus ester from esterification of 1H,1H-perfluoroundecan-1-ol with 2,5-furandione. The mass fraction for both types of coating was chosen to obtain 5–10% mass of the dry *nAl*. The coating process carried out for each chemical is summarized in Table 2. In addition, ultrasonication was used to achieve a better cohesion of the dissolved reagents with the particle surface and the destruction of particle clusters. The duration of the ultrasonication process (25 min) was selected on the basis of previous experimental results and literature data [25]. The summarizing scheme of particles passivation/coating is presented in Fig. 2.

Several physical parameters of *nAl* were measured to compare the difference between coated and uncoated *nAl* (Table 3). SEM (PHILIPS CM 12) and TEM (FEI QUANTA 200 3D) were used to characterize *nAl* particle shapes. The BET specific surface area (NOVA 2200 E) and active Al content [26] were evaluated as well. Non-isothermal oxidation (DSC-TGA, NETZSCH STA 449 F3) analyses were performed under air atmosphere at 10 °C/min heating rate.

3. Results and discussion

The diameter and length of the exploded wire (0.32 mm and 100 mm for the 100 nm samples; 0.25 mm and 80 mm for the 50 nm samples) are the main differences in the production parameters for the two *nAl* batches (Table 1). The detailed nomenclature of the