

Short communication

Aluminum nanopowders produced by electrical explosion of wires and passivated by non-inert coatings: Characterisation and reactivity with air and water

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Abstract

Results of the comprehensive characterisation of electro-exploded aluminum nanopowders, passivated with the non-inert reagents: oleic acid ($C_{17}H_{33}COOH$) and stearic acid ($C_{17}H_{35}COOH$), which were suspended in kerosene and ethanol, amorphous boron, nickel, fluoropolymer and Al_2O_3 (for a comparison), are discussed. Aluminum nanopowders with a protecting surface show increased stability towards oxidation in air and in water during the storage period. On the basis of the experimental results, a diagram of the formation and stabilization of the coatings is proposed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Aluminum nanoparticles; Stability; Water; Air; Passivation; Non-inert coatings; TEM; SEM; DTA-DSC-TG

1. Introduction

Metal nanopowders have been recently studied for the application in a wide variety of materials, e.g. ceramics as promoters for sintering processes of oxides [1], lubricants for micro-cracking recovering and tear decreasing [2], energetic materials as burning rate accelerators and hydrogen sources [3], in catalysis for hydrocarbon conversion [4]. The behavior of metallic nanopowders in different media is mainly defined by their reactivity with air and water [5], because traces of these substances are present almost everywhere: during the period after production and before application, the powders often come into contact with such oxidizing media. Hence, a lot of studies, devoted to this problem, were published [6], but the problem of the protection of the surface of the metal nanoparticles seems to

be one of the most important for the development of applications for industrial metallic nanopowders [7].

This work is mainly focused on the protection of aluminum nanoparticles used in energetic materials. Recently, aluminum nanopowders (ANPs), produced by an electrical explosion of wires (EEW) method, are most propagated in the world market [8]. This method has a lot of advantages compared to others [9]: high productivity (100–200 g of ANPs/h for each machine) and low cost of the powders because electrical energy is consumed for the metal wire destruction only (no additional plasma sources, no vacuum and cooling system). After the production, the reactivity of the surface of EEW-ANPs is extremely high: powder storage in an inert gas media results in self-sintering, thus particles should be passivated before the further treatment because non-passivated ANPs immediately self-ignite if exposed to air. The majority of commercially available ANPs are passivated by inert oxide layers consisting of amorphous or crystalline Al_2O_3 [10]. The mechanism of the stabilization of oxide layers on metal particles is widely studied [11]. In fact, the process of oxide layer formation on the surface of nanoparticles upon slow oxidation in air should be called “passivation-up-to-self-saturation” (the structure of such self-saturated oxide layers on Al nanoparticles produced by EEW, was studied in [11]). But the experimental approaches for the maximal metal storage in

Abbreviations: ALEX, aluminum explosive (TM); ANP, aluminum nanopowder; d_v , volume mean particle diameter, nm; C_{Al} , metal aluminum content, wt.%; DSC, differential scanning calorimetry; DTA, differential thermal analysis; EDS, electron diffraction spectroscopy; E/E_s , energy entered into the wire, a.u.; EEW, electrical explosion of wires; HTPB, hydroxy-terminated polybutadiene; SEM, scanning electron microscopy; S_{sp} , area of the specific surface, m^2/g ; TEM, transmission electron microscopy; TG, thermogravimetry; XRD, X-ray diffraction.

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Table 1
Properties of aluminum nanopowders studied

No.	Sample code	Initial wire composition	Gas media in explosive chamber	Passivation condition	S_{sp} (BET), m^2/g	a_v , nm	C_{Al} , wt.%
1.	ALEX	Al	Ar	Air	11.3	484	86
2.	Al (Ni)	Al (Ni)			40.7	237	53
3.	Al (B)	Al (B)			12.0	610	84
4.	Al (St Ac) ethanol	Al		Stearic acid in ethanol	12.1	255	74
5.	Al (St Ac) kerosene	Al		Stearic acid in kerosene	7.3	410	79
6.	Al (Ol Ac)	Al		Oleic acid in ethanol	14.3	393	45
7.	Al (F)	Al		Teflon	11.6	284	81

Al particles and comprehensive analysis of the processes, occurring during the particle passivation by different substances, should be developed. Treatment of the Al nanoparticles (ALEX[®]) in solutions of carboxylic acids [12] as well as synthesis of the hydrocarbon layers on particle surfaces [13] requires very special experimental conditions and does not result in significant advantages in metal content in particles after such treatment.

In the present work, powders were prepared by the EEW method and passivated by different substances: nickel, fluoropolymer, boron, stearic and oleic acid, suspended in kerosene and ethanol. This technique of coating particles by non-inert substances before they come into contact with air was selected because, when the oxide layer was already built up on particles (usually 10–20 wt.% of Al_2O_3), it cannot be removed or substituted under any kind of after-passivation treatment. The properties of the produced powders were comprehensively studied by several chemical analyses. Experimental data of the passivation and oxidation of EEW-ANPs in air and in water were accumulated and analyzed.

2. Experiment

ANPs were produced in argon atmosphere by using the EEW facilities developed by the High Voltage Institute at Tomsk Polytechnic University, Tomsk, Russia [9]. The initial Al wire, used for the production of the ANPs, was 0.27 mm in diameter and of 99.8% purity. The rate of wire feeding was about 50 mm/s and the explosions were repeated with a frequency of ~ 1.1 Hz. The optimal electric parameters, preliminary found, were $E/E_s = 1.4$, $U = 26$ kV, $L = 0.6$ μ H for the EEW machine UDP-4G. After producing 1–2 kg of powder, the collector with the powder was removed, and the working cycle was repeated. While the EEW machine was stopped, the collector with the powder was placed into a separate pressure tight passivation chamber. The list of samples, studied within this work, and their specific surface area (S_{sp}), determined by BET method, as well as the metal aluminum content (C_{Al}) after passivation, measured by volumetric analysis, and the volume mean particle diameter (a_v)

Table 2
Elemental and phase composition of aluminum nanopowders

No.	Sample code	Wt. content of elements, % (EDX)			Phase composition (XRD)
		O	Al	Ni	
1.	ALEX	10	90	–	Al
2.	Al (Ni)	22	74	4	
3.	Al (B)	11	89	–	
4.	Al (St Ac) ethanol	15	85		Al, traces of Al_4C_3
5.	Al (St Ac) kerosene	15	85		
6.	Al (Ol Ac)	18	82		
7.	Al (F)	12	88		Al

are shown in Table 1. The “Zetasizer 2000” by Malvern Instruments, UK was used for the determination of the particle size distribution and the volume mean particle diameter (a_v).

Sample 1 (commercial powder ALEX) with widely studied characteristics [14] has been taken for comparison. Samples 2 and 3 were obtained from the composite wires Al–Ni and Al–B, respectively [15]. Air-passivation (samples 1–3) was carried out at $T = 30 \pm 2$ °C and $P = 1.1$ atm argon having an air content of about 0.1 vol.%. The ANP samples 1–3, Table 1, were completely passivated by an Ar/0.1 vol.% air mixture for 72 h. At higher concentration of air in the passivation gas mixture, self-heating and powder self-sintering occur.

Samples 4–7 were passivated by organic substances in solvents before they came into contact with air:

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

The solution for passivation was added to the fresh powder immediately after production and the powder solution was mechanically stirred for ~ 2 h. The temperature was maintained at

Table 3
Reactivity parameters of aluminum nanopowders ($m = 7.5$ mg) under non-isothermal heating in air

No.	Sample code	T_{ox} onset, °C	Weight of coating (gases), %	$+\Delta m$ (up to 660 °C), %	$+\Delta m$ (up to 1400 °C), %	ΔH_{ox} , J/g	α (500–1400 °C), %
1.	ALEX	558	2	26	68	5465	89
2.	Al (Ni)	565	9	13	43	–	88
3.	Al (B)	556	2	24	63	6232	84
4.	Al (St Ac) ethanol	549	5	23	58	5997	88
5.	Al (St Ac) kerosene	557	6	27	74	6282	105
6.	Al (Ol Ac)	486	10	15	38	4875	95
7.	Al (F)	538	6	21	68	5184	94

$$\alpha(Al \rightarrow Al_2O_3) = \frac{+\Delta m}{C_{Al} \cdot 0.89} \cdot 100, \%$$

C_{Al} , % — metal content in the samples (Table 1).

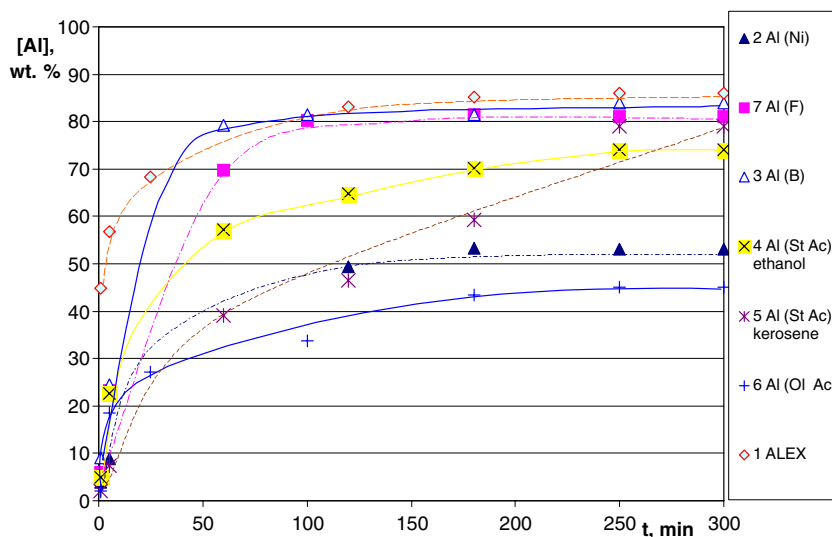


Fig. 1. Kinetic curves for aluminum nanopowders with different coatings, interaction with 10 wt.% NaOH water solution. Numbers of the samples in Table 1.

30 ± 5 °C in order to avoid self-heating of the powder. The residual solvent was evaporated from the ANPs by vacuum treatment at room temperature. All passivated powders were stored 2 months before analysis in the air with a humidity $RH \sim 75\%$ in closed banks for the simulation of industrial conditions.

The morphology and the compositions of particles (Table 2) were tested by TEM-EDS (Philips CM 200 FEG), SEM (JEOL 6500 F) and XRD (Rigaku “MAX-B” diffractometer) with CuK_{α} radiation. Two types of ANP-tests were used: reactivity in air (Table 3), and in 10 wt.% NaOH water solution (Fig. 1). DTA-DSC-TG (Universal 2.4 F TA Instruments) was used for testing the non-isothermal oxidation.

3. Results

The specific surface area was at the same level ($11\text{--}14$ m²/g, Table 1) for all samples except sample 2 (40.7 m²/g) and 5

(7.3 m²/g). The reduction of C_{Al} is maximal for ANP passivated by oleic acid — down to 45 wt.%. One of the possible reasons is the interaction of oleic acid with NaOH, resulting in a formation of the non-soluble sodium oleate layer, which protects the fresh metal from further oxidation in the selected experimental approach. Hence, the coating of particles by organic reagents leads to a considerable reduction of the specific metal content because the particles hold a lot of organic substances on their surface (Table 1). In the case of boron this effect is not so obvious. The term “specific metal content” (Table 1, last column) characterizes the content of metal in the powder, but not in the particle (Table 2). ALEX has a relatively high metal content and S_{sp} is comparable to sample 3 (boron coated).

According to TEM, the concentration of Al inside the particles increases when applying organic coatings (Fig. 2), while the specific metal content is lower for powders passivated by organic substances (Table 1). The content of metal in the particles,

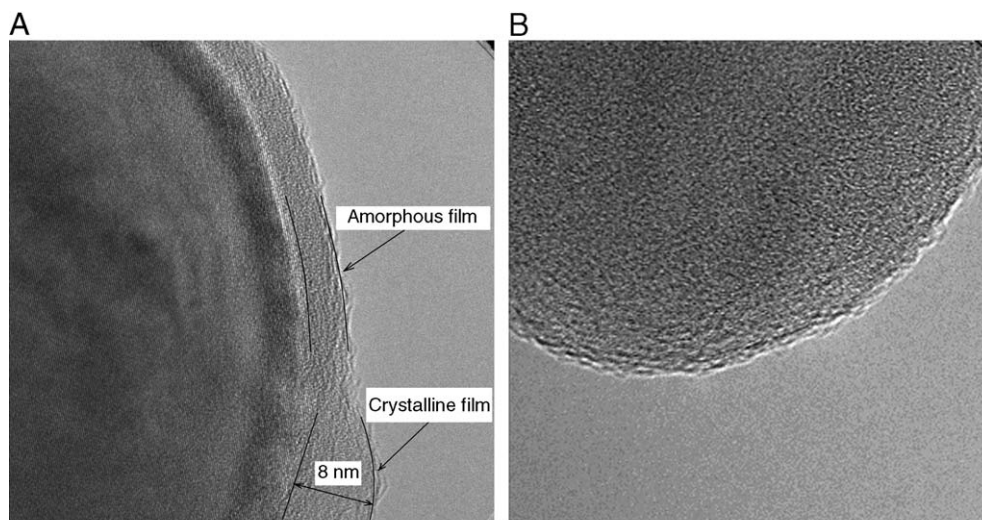


Fig. 2. TEM images of ANPs passivated by air (A, sample 1) and by oleic acid (B, sample 6).

passivated by oleic acid, is higher than for ANP passivated by air. According to TEM data, the particles, passivated by air, are covered by oxide films (thickness of 4–8 nm), while the particles, passivated by oleic acid (Fig. 2B), do not have any visible oxide layer. Analyzing the image in Fig. 2A, we can observe the beginning of oxide film crystallization, i.e. the critical thickness for amorphous oxide film is 4–5 nm after which crystallization begins. Thus, under selected air-passivation conditions, at the thickness of the oxide layer of 4–5 nm, the oxidation of the particle's surface stops and crystallization of the oxide layer occurs.

BET and a_v data from Table 1 do not correlate, that, probably, means the presence of a small amount of very fine particles too in samples, but even a small quantity of very fine particles determine the high value of S_{sp} . The diameter of the largest particles found was not more than 1–2 μm (by TEM, SEM and size distribution analyses) for all samples.

The results of EDS and XRD study are presented in Table 2. All powders contain more than 10 wt.% of oxygen (as oxides) on the particle surface. Traces of aluminum carbide were found by XRD for the samples 4–6, but carbon was not determined by EDS because carbon films were used as object slides for the samples. Boron in sample 3 was not found, probably because of its low molecular weight and, hence, EDS method has low sensitivity for this element.

The beginning of intensive ANP oxidation in air was below the melting point of aluminum (660 °C). The results of the DSC-TG analysis of the ANP samples in air are represented in Table 3. The non-isothermal heating of the samples was executed with a rate of heating 10 of K/min. The maximum temperature of the oxidation onset ($T_{ox\ onset}$) is characteristic for sample 2. Probably, this is caused by the presence of refractory nickel (see Table 2) in the composition of the passivating layer on the particles surface. The $T_{ox\ onset}$ of the samples, passivated by air, changes in the range of 556–565 °C and does not correlate with the dimensional characteristics of the powders and the type of the passivating coating. For sample 8, the oxidation begins at 486 °C (much lower than the melting point of aluminum). The adsorbed gas weight for the samples of “dry” ANP (samples 1–3) does not exceed 2% with exception of the nickel-containing sample. The mass of organic coatings (samples 4–7) is 3–4 times higher than for the “dry” samples 1–3. The degree of conversion (α) to 1400 °C (last column, Table 3) is relatively high for all samples.

The kinetics of the interaction of the powders with water was investigated using a 10% NaOH solution at temperature of 20 °C (Fig. 1). The kinetic curves for all powders have the same character, but ALEX does practically not have induction period. The coated ANP samples show a good stability in the NaOH solution. Thus, practically each of the organic coating protects the particle surface against oxidation in water better than oxide ones.

4. Discussion

The specific metal content for ALEX is the highest compared to the other powders. The reaction of the “dry” powders with NaOH water solution has no induction period (Fig. 1). Hence, the oxide film has low protective properties in water.

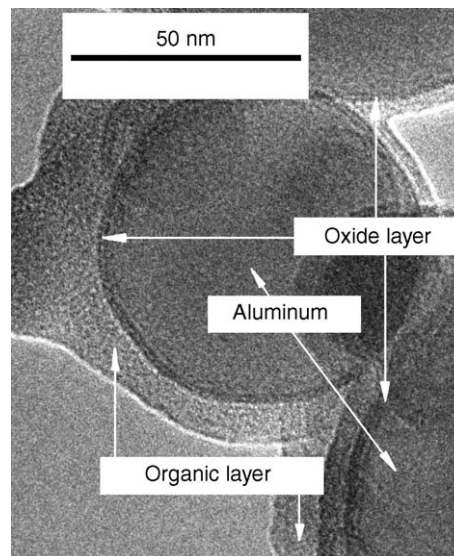


Fig. 3. Two-layer coating of organically passivated Al particles.

According to TEM, the sample Al (Ni) consists of two types of particles: a very fine fraction and large particles. 4 wt.% of Ni (Table 2), according to EDS, do not cover the surface of the large Al particles, but are separately distributed in a small oxidized fraction. The particle surfaces of this sample are not smooth. Thus, the explosion of Al–Ni composite wires results in the formation of the smaller particles (Table 1) than for Al without coating, but the size of such small particles is less than the border of stability — about 30 nm for Al [7]. The residual non-oxidized Al particles react with air completely at $T < 1000$ °C (Table 3): Ni does not increase the stability of fine Al particles towards oxidation in air.

The aluminum content and S_{sp} for the sample Al (B) was nearly the same as for sample 1 (ALEX, Table 1), and the degree of conversion up to 1400 °C is high enough (Table 3). Boron-coated powder has also a high value of ΔH_{ox} in air. Boron-coated particles react with water having a very short induction period (few seconds, Fig. 1). Ni-coated particles have a low Al metal content under reaction with water. It can be caused by the presence of a lot of NiO and a big fraction of very fine oxidized particles.

Stearic acid and oleic acid mostly interact chemically with the aluminum particle surface during passivation. In the case of oleic acid, interaction with metal was more intensive C_{Al} decreased to 45 wt.% in sample 8 (Table 1). It is noticeable that the interaction of Al with stearic acid and oleic acid results in the carbidization of the particles surfaces (see Table 3). For the majority of the organic-coated particles, we did not observe strong organic layers which could completely protect Al particles from further oxidation. In the case of Al (OI Ac), the particles hold more oxygen than other samples (Table 2). Moreover, according to TEM, organic-coated metal particles have two layers: an organic layer and an internal oxide layer (Fig. 3).

5. Conclusion

The most important advantage of non-inert-coated aluminum nanoparticles is their expected higher combustion enthalpy

compared to Al₂O₃-passivated Al particles. The drawback of non-oxide coatings is the decrease of the specific metal content in the powders. For all organic-coated particles, the organic layer is transparent for oxygen and results in an internal oxide layer formation (Fig. 3). Aluminum particles, produced from composite Al (B) and Al (Ni) wires, show approximately the same characteristics as oxide coated.

Acknowledgments

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