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Air and water oxidation of aluminum flake particles

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ABSTRACT

The article deals with the oxidation of aluminum flake particles with specific surface area ranged from 0.37 m^2/g to 0.73 m^2/g. The investigated powders which consisted of the above mentioned flake particles contained metal aluminum in high values (95–98 mass %). The powders possess a high hydrogen release rate (up to 27 cm^3/min) by the interaction with calcium hydroxide water solution. The powders under study revealed a high reactivity while oxidized in a non-isothermal mode in air. The reactivity parameter values for aluminum flake particles can be compared to those of aluminum spherical nanoparticles. The application of these aluminum flake particles were possible in two directions due to their high metal content in combination with low specific surface area and high reactivity: pyrotechnics and cellular concrete production.

1. Introduction

Aluminum powders are applicable both for energetic materials and cellular (aerated) concrete [1–2]. For the powders as a scientific object it is important to understand their oxidation behaviour both in air (for storage and transportation) and in water-based alkaline solutions (for the applications in cellular concrete and hydroreactive fuels).

Aluminum flake-particle powder (further "f-Al") is produced on a tonnage scale and used in pyrotechnics [1], paint-and-lacquer coating and construction industry for cellular concrete production [2]. The f-Al is used in the construction industry as pore-forming reagents in the cellular concrete production and they have no competitors in this sphere. The selection of a pore-forming reagent is based on the principle that the pores that are built in the cellular concrete should always have the same size. The reaction time for the chemical interaction of aluminum with calcium hydroxide solution should be optimally estimated. The high metal content and the high reactivity are two key factors for the f-Al application in pyrotechnics.

Aluminum spherical-nanoparticle powder (further "n-Al") has been thoroughly studied as the most challenging energetic material component [3,4]. Since 1990s the properties of the n-Al obtained by different methods have been investigated in all the details beginning with the studies in [5–6] till the comprehensive reviews on their properties and applications in [7–9]. There are numerous advantages of the n-Al usage in heterogeneous reactions. They are a high reaction rate, the completeness of n-Al reaction with oxidizers and a non-toxic nature of this material [7–9]. However, some serious shortcomings for the industrial application of n-Al obtained by high productive methods (i.e. wires electrical explosion) have been exposed:

- particle ageing and chemical degradation by polymer matrix [10] and air [11] storage;
- particles aggregation during production [12];
- metal content: <90 mass % compared to the micron-sized aluminum particles i.e. 98–99.5 mass % [11];
- low wettability of aluminum nanoparticles by resins [13].

The above mentioned lacks made the energetic community to find out some substitutions for the n-Al. The advanced energetic characteristics for the so-called "activated aluminum" were reported recently in [14]. However, the physical and chemical characteristics of the "activated aluminum" with the average surface particle-diameter of 5.5 μm is placed far behind of those for the n-Al ALEX with the average surface particle-diameter of 0.1 μm. Furthermore, the metal content in the "activated aluminum" is rather low (91–94 mass %). The burning rate of the lab-scale aluminized propellant samples based on hydroxyl-terminated polybutadiene and ammonium perchlorate with "activated aluminum" is only on 1–2 mm/s higher (4.5 mm/s vs. 3.5 mm/s at 10 bar) compared to the propellant loaded with micron-sized Al (further "μ-Al") [14].

At the same time, the flake shape of Al particles is not critical for many applications such as pyrotechnics, thermites and solid fuels [15] as well as for non-energetic applications [16]. This work is aimed to

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Table 1
Characteristics of aluminum particles f-Al (RA20 - RA60 grades).
PAP-2, ALEX, ASD-4 and A-Al01 properties are given for comparison.

Al type	Al sample	Metallic aluminum content, mass %	Specific surface area (by BET), m^2/g	Apparent density, kg/m^3	Content of particles, mass %		
					<10	<50	<90
					Particle size, μm		
f-Al	RA20	95	0.73	0.17	11	23	42
	RA30	96	0.54	0.17	15	35	71
	RA40	97	0.41	0.14	17	44	92
	RA50	98	0.40	0.13	19	50	107
	RA60	98	0.37	0.11	22	61	128
	PAP-2 [11]	94	5.40	n.a.			
n-Al	ALEX [11]	91	20.50				
	ALEX Al-1-50* [30]	90	15.70				
μ-Al	ASD-4 [14]	99	0.38				
	A-Al01 [14]	94	2.60				

* ALEX sample with the maximal value of its specific surface area (by BET) was taken from [30].

characterize the f-Al obtained by the method of molten aluminum streaming in nitrogen followed by the process of ball milling. The f-Al advantage is a high-tonnage production capacity [17].

The quality requirements to f-Al are increasing constantly [18]. On the example of the Russian powder market in 1980–1990s the most widespread gas-forming reagents for cellular concrete were aluminum powders of PAP-2[1] type [19]. Nowadays more new types of aluminum powders and pastes are being produced and to be found on the world market [20].

The aim of this work is to study physical and chemical properties of f-Al (RA20, RA30, RA40, RA50 and RA60 grades) and their reactivity while interacting with alkaline water solutions and with air. A comparative analysis of the f-Al characteristics with those of n-Al and μ-Al was fulfilled as well [11,14].

2. Experiments, results and discussion

2.1. Physical characteristics of f-Al

Five batches of f-Al powders (RA20, RA30, RA40, RA50 and RA60 grades) were produced by the method of molten aluminum streaming by SUAL-PM LTD (Russia, www.rusal.ru). The properties of f-Al samples were tested according to standard tests for aluminum particle characteristics: active (metallic) aluminum content was defined by means of the volumetric method, i.e. by measuring the released hydrogen volume during aluminum powder mixing with sodium hydroxide [21]. The specific surface area was studied by means of the BET adsorption method (Quantachrome Nova). Physical characteristics of f-Al (RA20-RA60 grades) are presented in Table 1 in comparison with PAP-2 powder (flake particles), n-Al (ALEX), μ-Al ASD-4[2] (spherical particles) and "activated aluminum" A-Al01 (spheroidal particles) [11,14,22]. The properties of the latter are well known and widely discussed [7,11,14].

The specific surface area of the samples of f-Al ranged from 0.37 to 0.73 m^2/g. These values were much less than those for 'activated aluminum' A-Al01 as well as those for n-Al ALEX. Active metal content for f-Al was by 1–4 mass % higher than that for 'activated aluminum' A-Al01 and by 4–7 mass % higher than that for n-Al ALEX. Table 1 illustrates the fact that the metal content in f-Al powder increases in the range from 95 to 98 mass % while their specific surface area decreases from 0.73 to 0.37 m^2/g respectively. These two parameters have a linear relationship and agree with the common regularities for the metal powders: the larger the particles, the higher is their metal content. The apparent density of f-Al varies in the range of from 0.11 to 0.17 kg/m^3 and is directly proportional to the BET specific surface (0.37–0.73 m^2/g). ASD-4 has nearly the same specific surface area as RA60. The fact is explained due to the powder morphology: in case of ASD-4 the particles were spherical, while f-Al had flake particles. PAP-2 has nearly the same metal content as RA20, at the same time its specific surface area is higher. Thus the size distribution curves for these powders are rather different. However, the BET values are easier to compare than the size distribution curves assuming that non-spherical particles tend to give significant errors concerning the size distribution curves due to the particle form factor [7].

Table 1, three last columns, presents the f-Al distribution curve according to the laser diffraction analysis executed by "Analysette 22" (FRITSCH, Germany): <90 mass % of particles in RA20 did not exceed 42 μm, while those in RA60 were not bigger than 128 μm. It should be mentioned, however, that the non-spherical shape of f-Al particles cannot provide a perfectly correct results for their size distribution curves.

2.2. SEM of f-Al

According to SEM images (JEM 2100F Jeol, Japan) various f-Al powders have nearly no difference in their morphology (Fig. 1).

The powder flakes possess a maximum size of ~50 μm. The thickness of the flakes is <1 μm. Thus, f-Al is a mixture of flake-shaped aluminum particles having a submicron thickness. The high-resolution SEM images (×1000) make it clear and visible (red arrows on Fig. 1).

2.3. Kinetics of f-Al oxidation by $Ca(OH)_2$ water solution

The rate of hydrogen release for f-Al samples was studied at the initial temperature of 25 °C. The powdery samples with their weight of 0.07 g were suspended in 350 ml of 2.5 mass % $Ca(OH)_2$ water solution and the suspension was being intensively stirred for 30 s. The reaction of the powders with $Ca(OH)_2$ water solution corresponded to the Eq. (1).

$$2\,Al + Ca(OH)_2 + 8\,H_2O \rightarrow CaO \cdot Al_2O_3 \cdot 6H_2O + 3\,H_2\uparrow + Q \qquad (1)$$

According to the Eq. (1) 1.5 mol of hydrogen (3 g or 33.6 l at standard conditions: temperature of 25 °C, atmospheric pressure of 1013 kPa) are gained from 1 mol of aluminum (27 g). Consequently, 0.087 l (87 cm^3) of hydrogen are gained from 0.07 g of aluminum. The results of the gas formation rate (Fig. 2) for f-Al samples in the $Ca(OH)_2$ water solution are shown on Fig. 3. This research does not analyse the solid reaction products. The Eq. (1) has been solely used to show that each mole of metallic aluminum gives 1.5 mol of hydrogen like in case with pure water. The redox reaction of metal Al with water in an alkaline medium is the only source for gas hydrogen in this interacting system.

[1] **P**udra **A**luminievaya **P**igmentnaya (pigment aluminum powder, Russian trademark) [11].
[2] **A**luminii **S**fericheskii **D**ispersnii (aluminum spherical dispersed, Russian trademark) [22].