

THE REACTIVITY OF Al-BASED “MECHANOCHEMICAL” NANOCOMPOSITES

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Abstract. The paper considers the rules of formation, the structure and reactivity of aluminum based composites with the additives of graphite, BN, MoO₃ and Teflon, prepared by mechanochemical method. Under mechanical treatment the following stages were separated: (i) independent grinding and mixing of reagents, (ii) formation of molecular-dense composites consisted from nanosized Al particles and matrix of second component, (iii) chemical interaction of components and (iv) crystallization of products. Formation of nanosized Al/X composites (stage ii) leads to the great increase of reactivity. For example, for Al/C nanocomposites the depth and oxidation rate of reaction of Al with oxygen, nitrogen and water significantly increases, but temperature of solid – phase interaction Al + C decreases down to 850 °C; for system Al/MoO₃ combustion rate increases from 1 to 400 m/s, for Al/Teflon was observed detonation-like regime with the velocity up to 1300 m/s, etc.

1. INTRODUCTION

Mechanical activation of materials in ball mills is a convenient and effective way to obtain nano-sized states [see for example 1-5]. This paper analyses the rules of formation under mechanical treatment, the structure and reactivity of aluminum based nano-sized composites with the additives of two types of solids: 1) layered materials (graphite and boron nitride) and 2) a set of materials, high aluminum oxidants (MoO₃, WO₃, Teflon). The last named compositions are energetic materials. The results obtained earlier for the Al/C system [6-10] were widely used in the present study.

2. EXPERIMENTAL

The mixtures of Al/X (X= C, BN, MoO₃, WO₃, Teflon) powders were mechanically activated by vibration or planetary mills. The details of specimen preparation procedure are described in [7,11]. The degree of the mechanical treatment was defined by the *D* dose (kJ/g) of applied energy [7]. The specimens were examined by X-ray diffraction, SEM, DSC, as well as the value of the BET specific surface. For the details of measurements and calculation of the coherent scattering domain size (*L*) see [10,12].

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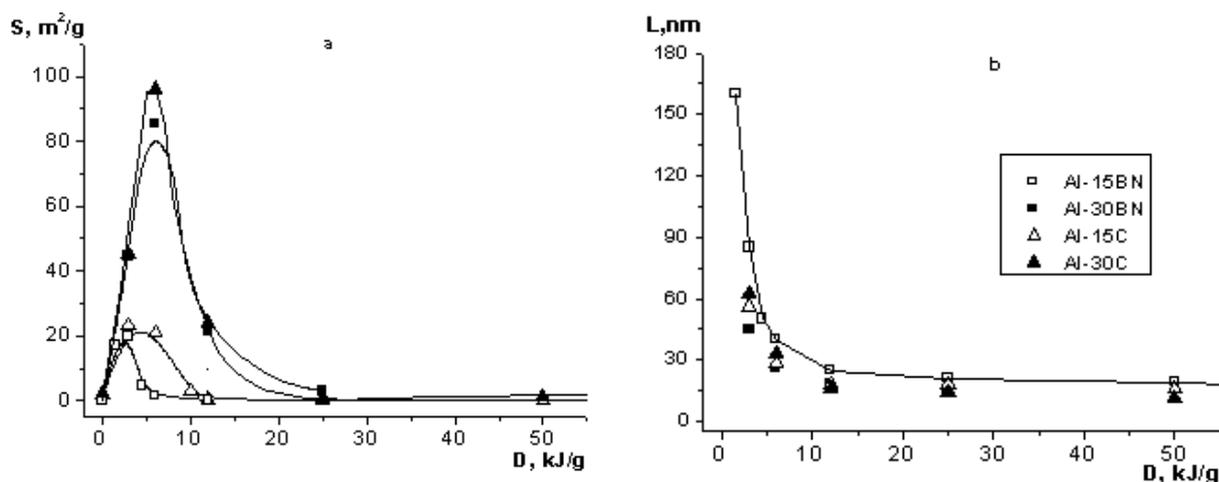


Fig. 1. Specific surface area (S) of Al-15wt.% BN, Al-30 wt.% BN, Al-15 wt.% C, Al-30 wt.% C (a) and coherent scattering domain size (L) of Al (b) under ball milling with dose D .

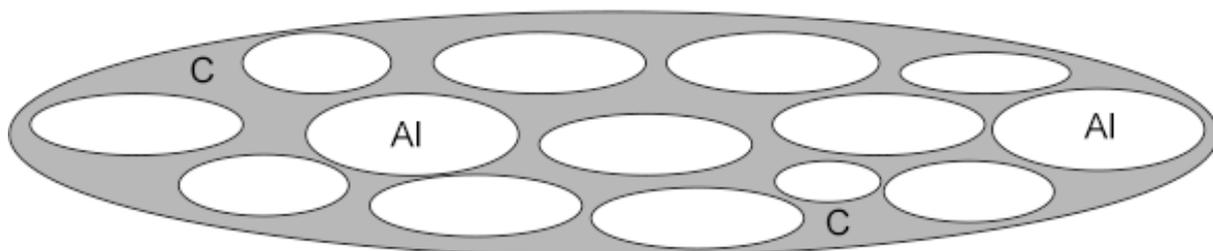


Fig. 2. Scheme of Al/X mechanochemically prepared nanocomposite Al/X ($X=C$, BN, MoO₃, WO₃, (-CF₂)_n).

3. RESULTS AND DISCUSSION

3.1. Formation of aluminum based nanocomposites and their structure

3.1.1. Al/layered material (C, BN)

The rules of formation of aluminum based nanocomposites are the most extensively studied for Al/C [6-10] and Al/BN two component mixtures. The additives concentration varied from 10 to 30 wt. %.

The following stages can be distinguished in the process of Al/C powder mixture mechanical treatment [10]: 1) grinding and blending of Al with graphite, the doses of applied energy $D < 5-8$ kJ/g, 2) molecularly-dense aggregation of the mixture and formation of nanocomposites, $D < 15-20$ kJ/g, 3) chemical interaction between Al and carbon, $D >$

20 kJ/g, 4) formation of the crystalline structure of the Al₄C₃ product, $D > 100$ kJ/g.

At the first stage, grinding (Fig. 1) and blending the components are of considerable importance. One observes a sharp growth of the mixture specific surface area (up to 100 m²/g, see Fig. 1a), which is determined by graphite grinding (for details see [6]). The coherent scattering domain size (L) of aluminum decrease (Fig. 1b), and aluminum passes into nanocrystalline state.

The beginning of the second stage is the point corresponding to a maximum on the $S(D)$ relationship (Fig. 1a). At the second stage, graphite transforms into amorphous state, but C atoms do not dissolve in aluminum (aluminum lattice parameter does not change), and there is no chemical interaction between aluminum and carbon. Decreasing the specific surface of the mixture is caused by physical coupling of aluminum and carbon into

Table 1. The list of investigated reactions of Al in mechanochemically prepared nanocomposites Al/X (X=C, BN, MoO₃, WO₃, (-CF₂)_n).

N	Reactions	System	Condition
1	$\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$	Al/C	Contact with air [6], Slow oxidation under heating [13], Shock wave oxidation [14]
2	$\text{Al} + \text{N}_2 \rightarrow \text{AlN}$	Al/C	Contact with air [6]
3	$\text{Al} + \text{H}_2\text{O} \rightarrow \text{AlOOH} + \text{H}_2$	Al/C	Oxidation by water at 50-90 °C [6,19]
4	$\text{Al} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2$	Al/BN	
5	$\text{Al} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2$	Al/C	"Explosive" oxidation at 90-100 °C [9]
6	$\text{Al} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Al}(\text{C}_2\text{H}_5\text{O})_3 + \text{H}_2$	Al/BN	
7	$\text{Al} + \text{C}_4\text{H}_9\text{OH} \rightarrow \text{Al}(\text{RO})_3 + \text{H}_2$	Al/C	At 90 °C Under milling
8	$\text{Al} + \text{C} \rightarrow \text{Al}_4\text{C}_3$	Al/C	1) Under milling [10] 2) Under heating [12]
9	$\text{Al} + \text{BN} \rightarrow \text{AlN} + \text{AlB}_2$	Al/C	1) Under milling 2) Under heating
10	$\text{Al} + \text{MoO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{Mo}$	Al/BN	Combustion [15,16]
11	$\text{Al} + \text{WO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{W}$	Al/BN	Combustion [15]
12	$\text{Al} + (-\text{CF}_2)_n \rightarrow \text{AlF}_3 + \text{C}$	Al/BN	Combustion, Shock wave initiation [11,17]

molecular-dense aggregates. As a result, the Al/C composite forms, in which active nanocrystalline aluminum is dispersed in a matrix of amorphous porous carbon.

Fig. 2 shows an imaginary scheme of Al/X nanocomposite. It is based on electron microscopy, X-ray and sedimentation measurements, first of all in the Al/C system [8]. It was found that the particles of chemically active Al/C composite are flaky porous aggregates with the average dimension up to 2.5-5 μm composed of aluminum nanocrystalline blocks with the dimensions about 15-60 nm; the aluminum blocks are dispersed in porous, amorphous carbon.

By the end of the second stage ($D= 15-20$ kJ/g), under impacts of the balls, the loose Al/C composite with the specific surface of tens of m²/g transforms to a powder having the specific surface of less than 1 m²/g (Fig. 1a) and the high Al/C contacts area. This state is favorable for the beginning of chemical interaction between Al and carbon. The formation of Al-C chemical bonds (the third stage) was controlled with the chemical analysis method by methane evolution at hydrolysis of the activated mixture [10]. Crystallization of the final product (Al₄C₃) (the fourth stage) starts only

when more than 2/3 of maximum possible amount of Al-C bonds has been formed in the amorphous phase; is registered by XPS method [10].

In the case of the Al/BN system, the process of nanocomposites formation is identical. Initially the specific surface of the system sharply increases up to tens of m²/g and then it decreases (Fig. 1a). The kinetics of decreasing coherent scattering domain size of Al is approximately the same in the both systems with layered additives (Fig. 1b). First microscopic data qualitatively confirmed the fact that the structure of the Al/BN composite is identical to the structure shown in Fig. 2. In the dose range from 10 to approximately 150 kJ/g, similarly to Al/C, we record only aluminum lines. At higher doses, we observe diffraction data of formation of AlN and AlB₂ products.

3.1.2. Mechanoactivated energetic composites (MAEC) (Al/Teflon, Al/MoO₃, Al/WO₃)

The mechanical treatment of energetic systems Al/Teflon, Al/MoO₃, Al/WO₃ is affected by a danger of explosion directly during ball milling. That is why ball milling was performed in the presence of the

Table 2. Comparison of reactivity of Al in mechanochemically prepared Al-based nanocomposites (Nano Al) and in initial Al before mechanical treatment (Initial Al).

N	Reaction	Parameter	"Nano" Al	Initial Al
1	Al + O ₂	Oxidation depth at 600 °C under "slow" heating [13]	43%	12%
2		Ignition temperature in shock wave [14]	400 °C	950 °C
3	Al + H ₂ O	Oxidation rate at 90 °C [9]	2.10 ⁻² s ⁻¹	1.10 ⁻⁴ s ⁻¹
4		"Explosive" oxidation [9]	Yes	No
5	Al + C	Temperature of carbide synthesis [12]	350 °C	1200 °C
6	Al + MoO ₃	Combustion rate [15]	400 m/s	< 1 m/s
7	Al + Teflon	Detonation [11]	1300 m/s	No

hexane. The explosion hazard restricts the ability to perform the tests at high doses and to study the kinetics in detail.

Fig. 3 illustrates SEM images of MAEC Al-55 wt.% Teflon with the dose of mechanical treatment of 8 kJ/g in back scattered electrons and Al characteristic radiation. The produced composite consists of flake particles of Teflon matrix with Al inclusion, i.e. its structure principally corresponds to Fig. 2, although comprehensive study of the composite structure and characteristic dimensions of its components has yet to be performed.

For MAEC Al/Teflon composition, aluminum particles are considerably encapsulated by Teflon and are beyond the reach of "external" molecules, e.g., water.

3.2. Reactivity of nanocomposites

Al-based nanocomposites produced by the mechanochemical method exhibit high reactivity. Table 1 presents the list of investigated reactions between Al and gases (reaction 1 and 2), liquids (reactions 3-6), and solids (reactions 7-11), while Table 2 compares interaction parameters in various processes for nanoaluminum and the same aluminum before mechanical activation.

Porous nanocomposites with the matrix composed of layered material (C, BN) have the maximum reactivity with gases and liquids.

3.2.1. Interaction with oxygen and nitrogen

High reactivity of aluminum in porous nanocomposites is demonstrated, first of all, by spontaneous ignition occurring at the first contact

of made up specimens and air (No 1 and 2 in Table 1). The products of quick ignition contain aluminum oxides and nitrides as well as aluminum carbide and aluminum carbonitride [6]. The procedure of mixture passivation was developed to prevent the ignition of activated specimens and to have a possibility for their storage [10].

The thermogravimetric method was used in [13] to compare oxidation of nanoaluminum and initial aluminum under heating in air at the rate of 10 deg/min. It was found that temperature of initial oxidation of nanoaluminum is 200 °C lower as compared to initial aluminum, while the oxidation degree at 600 °C is almost four times higher (No 1 in Table 2). Only aluminum oxides are found in the products of "slow" oxidation.

One more example of high reactivity of nanoaluminum was found in the experiments in a shock tube [14]. Ignition temperature in back shock wave appeared to be 550 ° lower for nanoaluminum as compared to non-activated aluminum (No 2 in Table 2).

3.2.2. Interaction with water and alcohols

Two modes of aluminum oxidation with water were recorded for Al/C and Al/BN systems (reactions 3 and 4 in Table 1). In the 50 °C < T < 90 °C temperature range nanoaluminum reacts with water in the quasi isothermal mode. Main products are hydrogen and bemitte AlOOH; Al(OH)₃ is produced in small quantities. On completing the induction period, the kinetics of interaction is adequately described with the law of diminishing sphere [9]. The effective activation energy of reaction equals 61 ± 10 kJ/mol, and does not differ from that for the speci-

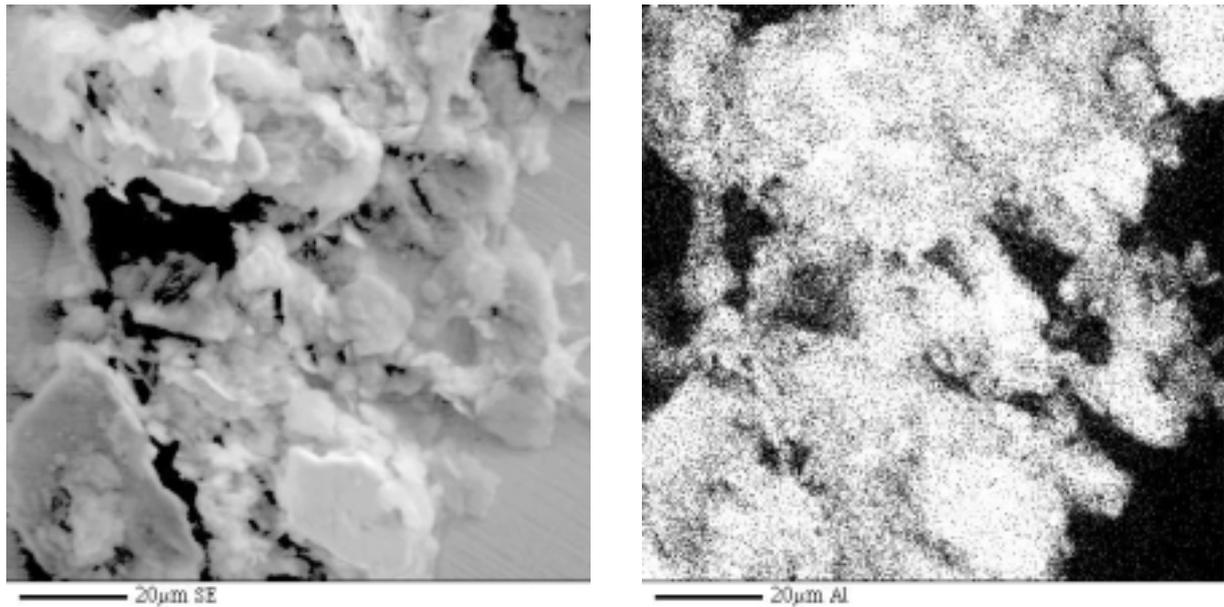


Fig. 3. SEM images (a) and corresponding area in aluminum characteristic emission (b) of mechanochemically activated Al – 55 wt.% Teflon mixture. The dose is 8 kJ/g.

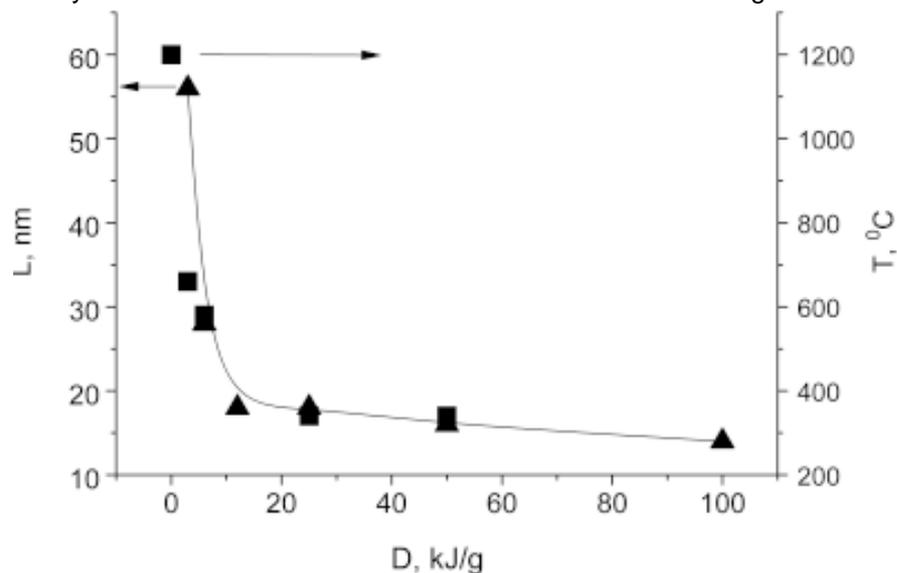


Fig. 4. Thermal synthesis of Al_4C_3 from mechanochemically activated Al-15 wt.% C under different dose D . L is the coherent scattering domain size for Al, T is the temperature of synthesis beginning.

mens of submicrone aluminum prepared by different ways. At temperature higher than 90-95 °C, the reaction turns into the thermal self-acceleration mode and explodes. In this case, oxidation of aluminum up to $\alpha\text{-Al}_2\text{O}_3$ is accompanied by exothermal reaction between aluminum and matrix material, in which aluminum carbide Al_4C_3 (for the Al/C system [9]) or aluminum nitrides AlN and Al_3N_4 (for the Al/BN system) are formed.

The rates of oxidation (and hydrogen evolution) for nanoaluminum are two orders higher than the rates of oxidation for non-activated aluminum (No 3 in Table 2). The conversion level can reach up to 90% (counting upon aluminum). This is why the above process may be of interest as a method for hydrogen production.

Interaction of activated Al with $\text{C}_2\text{H}_5\text{OH}$ is accompanied by hydrogen release (reaction 5 in Table

1). The reaction rate of Al with alcohol is lower than with H_2O almost by a factor of 10^2 and the depth of transformation is only 12%. First data were obtained on the explosive interaction of aluminum in nanocomposites Al/C with C_4H_9OH under ball milling (reaction 6).

3.2.3. Solid phase interaction Al+C, Al+BN

Section 3.1 gives brief descriptions of main stages of transformation of Al/C and Al/BN composites into final crystalline products Al_4C_3 , AlN and AlB_2 respectively in the process of mechanical treatment (reactions 7 and 8 in Table 1). The same final products can be produced by heating of "partially" activated compositions. It was found in [12] with the aid of DSC and X-ray methods that the mechanical treatment of the powders decreased the temperature of carbide synthesis by 800 °C, and the mechanism of synthesis changed from liquid-phase to solid-state. Fig. 4 correlates the temperature of synthesis beginning with the coherent scattering domain size (L) at various doses. Both curves coincide. Decreasing the temperature of synthesis occurs as long as L size decrease. Thus, the formation of "dense" nanocomposites is the most significant factor. Considerable decrease of the temperature of synthesis was also observed for the Al/BN system.

3.2.4. Mechanoactivated energetic composites (MAEC)

Chemical conversions in Al/Teflon, Al/MoO₃, Al/WO₃ MAEC (No 9-11, Table 1) were initiated by two ways – ignition or shock-wave action. High velocities (up to 300 - 400 m/s) [15,16] were reached in the experiments on burning. This is two orders higher than in the case of the mixtures with non-activated aluminum (No 6, Table 2). The obtained results on detonation have demonstrated the possibility of reaching the steady detonation regime in the Al/Teflon MAEC, in which the end products of detonation are in the condensed state (detonation velocity is up to 1300 m/s) [11,17]. It should be emphasized that it is impossible to obtain such regimes without mechanical activation (No 7, Table 2).

4. CONCLUSION

Aluminum based nanocomposites prepared by the mechanochemical method have increased reac-

tivity of their components in various processes. This may be used for the development of various energetic materials, materials for hydrogen power systems, cermets, etc. Formation of nanocomposites is the intermediate stage of the mechanochemical synthesis, and, depending on the formulated problem, one can prepare the specimens with different properties. For example, to accelerate the processes of aluminum oxidizing by water (to give hydrogen) or oxygen, it is favorable to prepare porous Al/C or Al/BN composites having the specific surface of 10-20 m²/g (i.e., the doses are 6-10 kJ/g, see Fig. 1). In order to obtain the maximum activation of the processes of thermal synthesis, e.g. aluminum carbide, it is necessary to have "dense" nanocomposites with the mixture specific surface lower than 1 m²/g (i.e., the reasonable dose is 15-20 kJ/g). The deeper mechanical treatment is not useful.

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