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Mechanochemically activated aluminium: Preparation, structure, and chemical properties

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Mechanical treatment of aluminium with 10–30 wt% graphite in the high-energy vibration mills leads to the formation of a chemically active substance. The structure of active aluminium and its formation are investigated by X-ray diffraction, adsorption, chemical analysis, and DSC. The reactivity of active Al is checked in reactions with graphite, as well as water, oxygen, and nitrogen. At the initial stage of mechanochemical interaction of aluminium with graphite, the dispergation of components and accumulation of defects in Al and C take place. Simultaneously, the surfaces of aluminium nanoparticles are covered with the carbon layer. Then the chemical interaction of aluminium with carbon starts on the surface of particles. At the final stage, aluminium carbide is formed in the volume of particles. The maximal reactivity of Al corresponds to the Al/C nanocomposites, in which chemical interaction of components is not yet realized. The reactivity of mechanochemically activated aluminium significantly exceeds that of standard aluminium powders. Interaction of activated Al with carbon takes place at 450°C, which is 800°C lower than the temperature at which the nonactivated aluminium reacts with carbon. Two types of reactions ("isothermal" and explosive) are observed for mechanochemically activated Al with water and air. © *2004 Kluwer Academic Publishers*

1. Introduction

Mechanical treatment of aluminium with graphite additives in high-energy mills resulted in chemical activity of aluminium in oxidation reactions with water or oxygen [1].

It is established [2], that carbides are formed during mechanical treatment of mixtures of various metals with carbon. In the case of the A1/C system [3], first, aluminium carbide forms, which later either transforms into an interstitial solid solution of carbon in the aluminium, or is converted to an amorphous phase.

The present report considers the variations in the crystalline structure of aluminium and carbon during physical and chemical interactions between them in the course of mechanical treatment of the mixture. Besides, we investigate the aluminium carbide synthesis on heating of the activated mixtures. Finally, the first systematic data on the reactivity of activated aluminium in the reactions with water, oxygen, and nitrogen are presented.

2. Experimental procedure

The mixtures of aluminium powder and carbon additives (10–30 wt%) were mechanically treated in a vibration mill [4] (10 steel balls, ball-to-powder mass ratio equal to 30, the volume of vial was 30 cm^3) under argon atmosphere. As local microanalysis showed the iron contamination does not exceed 0.5 wt% for a dose of about 10 kJ/g.

The magnitude of the specific dose of applied mechanical energy D (kJ/g) was used to characterize the mechanochemical impact. It was calculated from the relationship $D = I \cdot t$, where I is the energy intensity of the mill (W/g) and t is the duration of treatment. The I value was determined by the calorimetric method [5] and varied from 0.2 to 20 W/g.

After mechanical treatment with the doses of 5–15 kJ/g, we observed self-ignition of the powder when the Al/C mixture contacted the atmosphere. To prevent the oxidation, we passivated the specimens with hexane. For this purpose the powders were either unloaded in the hexane medium, or additionally treated in the presence of hexane.

The specific surface area of the powders was measured by the argon absorption at 77 K and calculated using the BET equation.

The X-ray diffraction measurements were recorded using the DRON-3 with Cu K_α radiation. The phase composition of the powders, the dimensions of the regions of the coherent scattering L(RCS), and the microdistortion magnitudes (ε,%) were determined by means of a procedure similar to that used in the study reported in [6].

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The formation of A1—C interatomic bonds was recorded with the chemical analysis method using the composition of the gas released on the mixture solution in water. On the pure aluminium solution, hydrogen is released (A1 + $2H_2O \rightarrow$ A1OOH + $3/2H_2$), while methane is released in the analogous reaction with aluminium carbides ($Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$). The content of Al—C bonds in the Al/C mixture was calculated with the methane portion in the gas released during oxidation. The composition of gases was determined chromatographically.

The DSC-7 (Perkin-Elmer) device was applied for the differential scanning calorimetry measurements (DSC), with the heating rate of 20 degrees per minute.

The kinetics and the degree of interaction between aluminium and water were determined by the volumetric method recording the release of gas in a closed volume.

The aluminium powder (PAP-2) was used as initial aluminium. The powder had particle dimensions of 5–35 μm and the specific surface area of 2.7 m^2/g. The initial synthetic graphite (MPG) had the specific surface area of 2 m^2/g.

2.1. Mechanochemical reaction of aluminium with carbon

2.1.1. Specific surface area

As the dose of the mechanical treatment increases, the specific surface area *S* of the (Al-25 wt% C) mixture increases too to about 50 m^2/g (Fig. 1, curve 1). The dose of about 6 kJ/g corresponds to the *S* maximum. The magnitude of *S* decreases as the dose further increases.

Curve 2 in Fig. 1 shows the variation of *S* for pure initial graphite on its mechanical treatment under the same conditions. First, *S* of the graphite linearly grows, reached its maximum (about 300 m^2/g) at the 10 kJ/g dose, and then it decreases.

Comparing initial portions of Curves 1 and 2 (Fig. 1) one can see that the points for both cases fall into the common straight line. Therefore, the specific surface area of the (Al-25 wt% C) mixture is about 1/4-th of the specific surface area for pure graphite. Thus, at the doses up to 4–5 kJ/g the increase of specific surface area of the mixture is mainly determined by the graphite crushing. At the doses above 6 kJ/g, the mixture specific surface area decreases. This points to the agglomeration of Al/C particles into dense aggregates. At a dose of about 35 kJ/g, the specific surface area of the mixture with 30 wt% of graphite is 2.8 m^2/g, while at a maximum dose of 92 kJ/g the specific surface is only 1.5 m^2/g (specimens 3 and 4 in Table I).

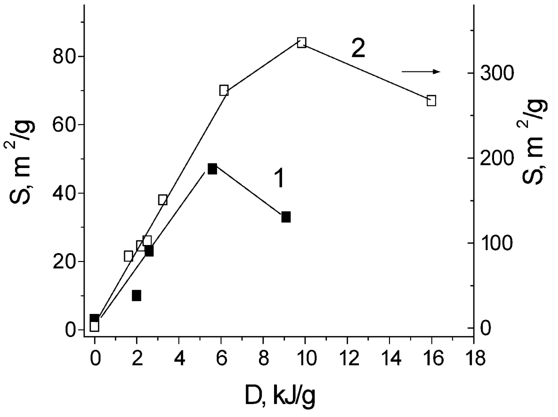

Figure 1 Specific surface area (*S*) of Al/C mixtures (1) and graphite (2) under the mechanical treatment with dose D.

TABLE I Specific surface area (*S*), structural parameters (a (Al), L(RSC)), and the results of chemical analysis for the Al/C mixture after mechanical activation at dose *D*. a (Al) is the lattice parameter of Al. L(RSC) is the dimensions of the region of coherent scattering of Al. [CH_4] is the part of methane in gas products of the mixture oxidized by water

N	*D* (kJ/g)	*S* (m^2/g)	*a* (Al) (nm)	L(RSC) (nm)	[CH_4] (%)
Initial	0		0.4049	>150	
1	8.7	40 ± 2	0.4049	73 ± 25	0.2 ± 0.1
2	10	13 ± 1	0.4051	52 ± 18	
3	35	2.8 ± 0.2	0.4049	21 ± 5	17 ± 2
4	92	1.5 ± 0.1	0.4052	20 ± 5	
1-T	8.7 + 500 C		0.4058	>150	
3-T	35 + 500 C		–	–	94 ± 5

2.1.2. X-ray diffraction

Fig. 2 illustrates the X-ray diffraction patterns of Al/C powders after mechanical activation. The lines of aluminium and graphite are observed in the X-ray patterns. As the dose of mechanical treatment increases, the graphite 002 line widens, its maximum moves towards small angles (i.e., the graphite interlayer distance 002 increases), and, then, the line disappears. At the 8.7 kJ/g dose, for example, only 1/4-th part of the initial graphite remained as a crystalline phase. The thickness of graphite crystalline blocks reduces up to 1.5–2 nm.

Only the aluminium lines are observed in the X-ray patterns for higher doses. At last, in the case of the specimen with the 92 kJ/g maximum dose, the X-ray

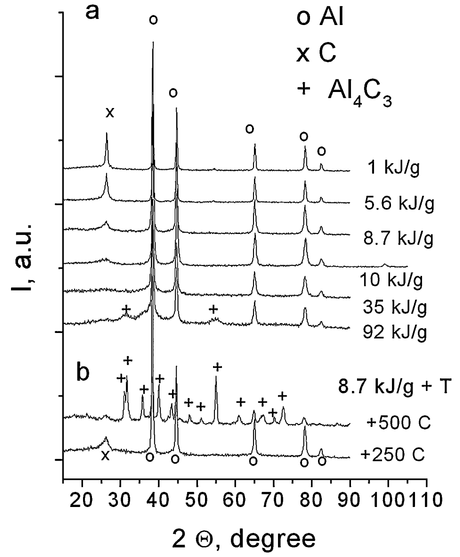

Figure 2 X-ray diffraction patterns of Al/C mixtures after the mechanical treatment with different doses (a) and annealing (b).

patterns show new broad lines along with aluminium lines. The new lines correspond to aluminium carbide Al_4C_3.

The magnitude of the aluminium lattice parameter increases with the dose, and at the 92 kJ/g maximum dose it reaches the value of 0.4052 nm (Table I). The increase of the lattice parameter may be related to the formation of the interstitial solid solution of carbon in aluminium. With data from [3], the maximum concentration of interstitial carbon is estimated at ∼2 wt%.

As the dose increases, the dimensions of the regions of coherent scattering L(RSC) decrease and at the 35 kJ/g dose, they reach the magnitude minimum of ∼20 nm (see Table I). The subsequent mechanical treatment (up to the 92 kJ/g dose) is not accompanied with a decrease in the L(RSC) dimension.

2.1.3. Chemical analysis

To estimate the amount of aluminium carbide in the powder, we applied the method of chemical analysis based on the measurement of the composition of gaseous medium formed during the reaction of specimen with water.

The last column of Table I presents the results of chromatographic analysis of the gaseous product formed during the reaction of specimen with water. At the initial stage of mechanical treatment (specimen 1 in Table I, the dose 8.7 kJ/g), the remaining graphite phase (5%) is still observed in the X-ray patterns. At this stage, the methane content is insignificant (0.2%) in the releasing gas product. This points to the likely absence of aluminium carbide in specimen 1.

At the following stage of the mechanical treatment, at the 35 kJ/g dose, the methane content in the gas phase is 17% (specimen 3 in Table I). This value indicates that about 30% of aluminium atoms are present in the specimen 3 in the "carbide" form. However, it should be noted that only aluminium lines are observed in the X-ray diffraction pattern of this specimen, i.e., aluminium carbide has not yet formed a crystalline phase.

2.2. Formation of aluminium carbide on heating of activated mixtures

The DSC and X-ray diffraction methods were applied to observe the formation of aluminium carbide on heating the activated mixtures. The tests were performed with two specimens (1 and 3 in Tables I and II) corresponding to the initial and intermediate stages of mechanochemical synthesis.

TABLE II Phase composition of the Al/C mixture after the mechanical activation and annealing. The symbols (+) or (−) correspond to the presence or absence of this phase

N from Table I	Composition	T (C)	Phase composition (wt%)		
			C	Al	Al_4C_3
1	Al-20 wt%C	20	5 ± 2	95 ± 5	–
		400	+	+	–
		500	5 ± 2	19 ± 2	76 ± 3
		700	7 ± 2	18 ± 2	75 ± 3
3	Al-30 wt%C	20	–	100	–
		500	–	–	100

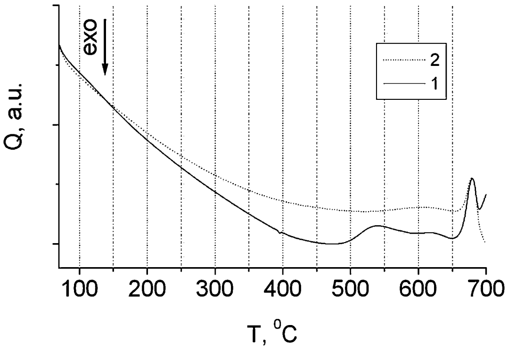

Figure 3 DSC curves of the mechanically activated sample 1 (Table I). Curve 1 is for initial heating, Curve 2 is for second heating.

Fig. 3 illustrates primary data on the heat evolution for specimen 1. Curve 1 corresponds to initial heating, while Curve 2 corresponds to repeated heating of the same specimen. It can be seen, that there is an endothermic maximum at about 660°C for both heating processes. This maximum corresponds to the temperature of aluminium melting. At temperatures below 650°C, the thermogram of repeated heating was used as the base line.

In addition to the endothermic maximum of aluminium melting, we recorded two exothermal peaks on the DSC curve at 450 and 600°C. To explore the nature of heat-evolution processes, we measured the X-ray diffraction patterns of the specimen after heating up to various intermediate temperatures (Fig. 2b and Table II).

As it is seen from Table II, initial aluminium and carbon remain in specimen 1 up to 400°C, while in the temperature range of 400–500°C aluminium carbide is formed. Thus, the exothermal peak at 450°C can be associated with the thermally induced formation of aluminium carbide.

The dose of the mechanical treatment for specimen 3 (Table II) is significantly higher as compared to that for specimen 1, and only widened aluminium lines are seen in its X-ray patterns after the mechanical treatment. There is only a single wide exothermic peak at 450°C on the DSC curve of specimen 3, and the X-ray analysis shows only aluminium carbide lines after heating up to 500°C (Table II). Thus, on heating the specimen, the complete thermal effect is determined by the formation of aluminium carbide. The magnitude of the thermal effect is 1.13 ± 0.05 kJ/g which corresponds to 163 ± 15 kJ/mole of carbide. In accordance to the data reported in [7], the heat of carbide formation equals 195 kJ/mole, hence, the degree of conversion can be estimated from the calorimetric data as approximately 80%.

The methods of chemical analysis confirmed the complete degree of conversion of the aluminium into carbide. Gas evolving on hydrolysis of the specimen appeared to be 94% methane (No 3-T in Table I). This means that 97% of aluminium atoms are chemically bonded to carbon.

In summary, for specimen No 3 (Table II) we obtained the following: about 20–30% of aluminium carbide were formed during the mechanical treatment process, while remaining 70–80% of carbide were formed upon subsequent thermal treatment.

2.3. Reactivity of activated aluminium in reactions with water and oxygen

The interaction of mechanochemically activated aluminium with water starts at temperatures higher than 50°C. Within a 50–90°C interval, the reaction can be performed under formal isothermal conditions. During contacts with water at 95–100°C, the reaction becomes self-accelerating and is transformed to the explosive mode. We shall first consider the results recorded under "isothermal" conditions.

2.3.1. "Quasi-isothermal" reaction of aluminium oxidation with water

Hydrogen is released during reaction of aluminium with water, that is why the kinetics and degree of conversion were mainly recorded by means of the volumetric method.

Fig. 4 illustrates typical curves of hydrogen release during the reaction between the mechanochemically activated aluminium and water (the methane addition in the released gas did not exceed 0.5% for the doses lower than 15 kJ/g; see, for example, specimen 1 in Table I). The following stages are apparent: the induction period, the reaction itself, and the saturation. Three curves correspond to different doses of preliminary mechanochemical treatment. With increasing dose of the mechanical treatment, both the slope of the curves and the degree of conversion grow. Maximum degree of conversion (0.82) is reached under 8–10 kJ/g doses. With the following increase of the dose, the amount of releasing gas decreases, and a noticeable amount of methane appears in the released gas.

Pseudobemite AlOOH is the main solid product of the reaction (Table III). The X-ray diffraction lines of the AlOOH phase are very broad, and the estimation for the dimensions of L(RCS) (with the Sherrer formula) gives the magnitudes of ∼50 Å. The specific surface area of oxidation products is about 130 m^2/g for specimen 3 (see Fig. 4). So the quasi-isothermal reaction of aluminium oxidation with water proceeds in the following way:

$$2\text{Al} + 4\text{H}_2\text{O} \rightarrow 2\text{AlOOH} + 3\text{H}_2 \qquad (1)$$

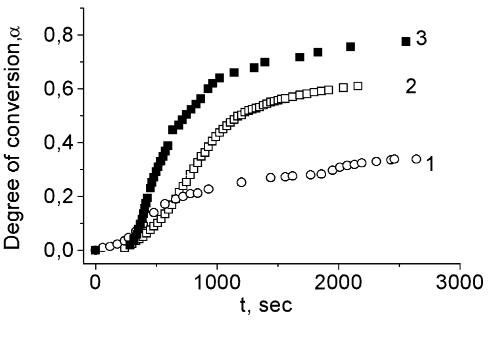

Figure 4 The kinetics of "isothermal" interaction of Al with H_2O (Reaction 1) at different stages of mechanical activation. The doses of mechanical treatment are equal to 2 (1), 8.7 (2), and 10 kJ/g (3). Temperature is equal to 75°C.

TABLE III Phase composition (wt%) of the mechanochemically activated Al/C mixture after interaction with water and air. The symbols (+) or (−) correspond to the presence or absence of this phase

	Type of reaction	Al	AlOOH	Al_2O_3	C	Al_4C_3	AlN, $Al_6N_2C_3$
H_2O	"Isothermal"	−	∼100	−	+	−	−
	Explosive	4	−	48	5	43	−
Air	Slow annealing	−	−	100	−	−	−
	Explosive	+	−	+	+	+	+

For comparison, we oxidised the initial aluminium powder (before the mechanical activation) under the same conditions. It has been found that the initial specimen reacts with water only at temperatures above 95°C. The rate of the oxidation reaction was 3 orders of magnitude lower as compared to the rates of oxidation reaction involving the activated specimens.

2.3.2. Explosive oxidation with water

At temperatures above 90°C, water oxidation of mechanochemically activated aluminium transforms to the explosive mode. In the process, we heard a pop and saw red-white luminous radiation. The following products are observed among combustion products: aluminium α-oxide (corundum), aluminium carbide, as well as un-reacted aluminium and graphite (Table III). Thus, when transforming to the explosive mode, aluminium oxidation follows the following reaction:

$$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \alpha\text{-Al}_2\text{O}_3 + 3\text{H}_2 \qquad (2)$$

Besides, aluminium reacts with carbon, and aluminium carbide is formed according to the following reaction:

$$4\text{Al} + 3\text{C} \rightarrow \text{Al}_4\text{C}_3 \qquad (3)$$

The third line in Table III shows the results of the quantitative phase analysis of reaction products. The data show that only 48% of aluminium atoms were involved in the oxidation reaction, whereas more than 40% of aluminium atoms were bonded to carbon. Two thirds of carbon atoms were used to form aluminium carbide, while about one third of carbon remained as graphite. Despite the presence of "free" carbon and surplus water, about 4% of aluminium atoms remained unbound.

The specific surface area of the powder decreased more than for two orders of magnitude in the explosive oxidation process. The fine powder changed to small sintered granules with the specific surface lower that 0.1 m^2/g.

2.3.3. Oxidation in air

As it was discussed in Section 2, freshly prepared Al/C specimens at 5–15 kJ/g dose spontaneously ignite in contact with atmosphere, and special measures were used to passivate the powders. The last line in Table III shows the phase composition of oxidation products after ignition in air. In this case, aluminium nitrides and carbonitrides were formed, along with aluminium oxide and carbide, i.e., there was a chemical reaction not only with oxygen but also with nitrogen present in air.

3. Conclusion

Mechanochemical activation of aluminum with graphite is accompanied by a considerable increase in aluminum reactivity. There are four stages in the mechanochemical reaction between aluminum and carbon: (1) independent milling of aluminum and carbon; (2) mixing the components with the formation of the block-mosaic aluminum structure and carbon distribution along intergrain boundaries of aluminum; (3) chemical reaction between aluminum and carbon with the accumulation of Al—C bonds; (4) formation of the aluminum carbide crystalline phase. The second stage appeared to correspond to the maximum chemical activity of aluminium (the doses about 10 kJ/g). The increase in the reactivity of aluminium is observed in its oxidation by water and oxygen. The mechanically activated formation of aluminium carbide takes place at 450°C, which is 800°C lower than the temperature at which the nonactivated aluminium reacts with carbon.

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