
**SELF-PROPAGATING
HIGH-TEMPERATURE SYNTHESIS**

**Fabrication of Metallic Powders for Energy-Intensive
Combustible Compositions by Mechanochemical Treatment:
1. Peculiarities of the Structure and State of Aluminum Powder
Particles Formed by Mechanochemical Treatment**

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Abstract—The morphology, dispersion, structure, and average particle size of aluminum powders after mechanochemical treatment with different organic modifiers (graphite, stearic acid, and polyvinyl alcohol) are investigated by electron force microscopy, X-ray phase analysis, IR spectroscopy, EDX, and granulometric analysis, which show significant changes in the particle surface layer. It is stated that the mechanochemical treatment of aluminum with organic additives leads to the partial reduction of the surface oxide layer and several types of active centers able to enter chemical reactions when using these composites in the composition of various combustible mixtures are formed. It is found that upon an increase in the content of modifiers, i.e., graphite and polyvinyl alcohol, in the composite with these additives, the activity of aluminum increases. The increment of the activity index falls with an increase in the content of stearic acid in the Al composite. This may be because a dense encapsulating layer poorly soluble in alkali is formed when grinding the Al–C₁₇H₃₅COOH mixture with a large amount of stearic acid (more than 5%). Both the accumulation and redistribution of defects over the particle bulk, an increase in amount of active aluminum, and the formation of active centers and the encapsulating layer based on organic modifiers occur during the mechanical action in powders of the compositions under study.

Keywords: mechanochemical treatment, aluminum, modifier, graphite, stearic acid, polyvinyl alcohol, composite, active centers

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INTRODUCTION

Mechanochemical treatment (MCT) occupies an exclusively important place among the multitude of methods of affecting the solid body in order to change its state; structure; and, correspondingly, properties, in particular, reactivity, and constitutes the basis of many manufacturing processes of materials with specified properties [1, 2]. When processing materials in mills, the trituration of the particles is accompanied by a change in their energetic state, i.e., activation, and the interaction between the mixture components, which results in the synthesis of new materials [3]. Dislocations are formed and migrate in the triturerated material during the MCT in highly energy-intensive mills, and the regions of microplasticity with the partially destroyed structure appear. Cracks are formed and developed after the elastic and plastic deformation

of the particles, which causes the destruction of the solid body (i.e., trituration). Herewith, interatomic bonds break, and a fresh surface is formed. The appearance of the highly active short-lived state on the surface, breaking of the chemical bonds, and an increase in the surface during the powder trituration, separately or all together, can cause the chemical interaction between the components of the triturerated mixture [3–5].

All processes of the structural reconstruction and chemical interaction start on the surface, while the rate of heterophase reactions is known [1] to be proportional to the surface area of the solid body. It is enriched by defects and radical centers, which enter various interactions with gaseous, liquid, and solid components, leading to the change in the surface structure (i.e., modification) due to their high reactivity.

The broad abilities of the MCT, in which nonthermal low-temperature reactions prevail, are illustrated by the fact that refractory substances and intermetallic compounds, inorganic and organic compounds were synthesized in the solid phase without the dissolution or melting of reagents, and new composition materials were formed [2, 5–7]. It is proven that various energy-enriched intermediate states, with the further decomposition of which a considerable part of heat is liberated, appear first and foremost during the deformation and destruction of solid bodies. The so-called black box occurs between the work and heat, and if the energy is supplied to it more rapidly than it is converted into heat, then various and unexpected chemical transformations can be realized [8].

Modification of powder particles directly during trituration is one of the MCT directions of inorganic materials [2]. This process makes it possible to simultaneously bring the material to the required degree of dispersity, dedicatedly form various surface centers, modify the surface and dispersed particles, and acquired plastic well-formable masses. The MCT extends the spectrum of modifiers used. The volume of research and publications in press, as well as presented at international conferences on mechanochemistry, grows each year, which reflects the prospects and efficiency of studies in this direction [9–11].

Much attention has been paid in recent decades to the use of the MCT of metallic powders, including aluminum ones [12, 13]. Such interest is caused by their application in various energy systems. However, the dense oxide film on the surface of aluminum particles hampers the ignition of compositions, which causes the low combustion rate. To remove the oxide film or decrease its thickness, different methods are applied, one of which is the MCT [14, 15]. Not only does the particles size decrease during the MCT, but the contact area between the reagents increases, the oxide film is removed from the particle surface, and defects are accumulated in the material volume (providing an increase in the chemical activity of powders). Herewith, it is important to choose the optimal processing conditions of powders in the mill: the time, ratio of weights of balls and powder, and the type and mass fraction of the modifying agent.

The goal of this study was to investigate the structural changes of the surface layer and chemical activity of aluminum powder particles during the MCT with various modifying additives, which promote the trituration of metallic particles, the change in surface morphology and composition, and the increase and stabilization of the active state of aluminum.

EXPERIMENTAL

Investigations were carried out using aluminum powder of PA-4 grade with an average particle size of 50 μm . Graphite (C), polyvinyl alcohol ($\text{C}_2\text{H}_3\text{OH}$)_n

(PVA), and stearic acid $\text{C}_{17}\text{H}_{35}\text{COOH}$ (SA) served as an organic modifying reagent.

The MCT was performed in a Pulverisette 5 centrifugal planetary mill (CPM) (FRITSCH, Germany): the steel working chamber volume is 500 cm^3 , the revolution rate is 400 rpm, and the acceleration is 40 g. Steel balls were used to triturate the powders. The treatment was performed in air with the weight ratio of powder and balls $M_p/M_b = 1/4$. The amount of modifying additives was varied during the trituration (3–20%). The process time was 20 min—this is the optimal value to exclude self-ignition and was selected by the results of previous investigations [16, 17]. To prevent the oxidation of aluminum particles by air oxygen after the MCT and evaluate the variations actually associated with the mechanical effect, the samples of the dispersed mixture were passivated with hexane (C_6H_{14}).

RESULTS AND DISCUSSION

Figure 1 shows the electron microscopy image, energy dispersive spectrum, and weight fraction of elements of the initial aluminum powder. The Al particles are spherical, and, according to the results of the energy dispersive analysis of the initial powder, the amount of metallic aluminum is 89.93 wt % and that of oxygen is 10.67 wt %. The presence of oxygen atoms evidences the presence of a rather dense oxide film on the particle surface.

The particles have a platelet (scaly) shape of different thicknesses after the MCT of aluminum with graphite and PVA. The Al particles treated in the presence of SA remained partially spherical (Fig. 2).

The amount of oxygen after the MCT does not exceed 2.96% in the Al–3% C composite, 3.34% in the Al–($\text{C}_2\text{H}_3\text{OH}$)_n composite, and 3.93% in the $\text{C}_{17}\text{H}_{35}\text{COOH}$ composite according to the results of the EDX analysis. The oxygen content in the initial Al powder was 10.67% and, consequently, its particles in the surface oxide layer partially reduce during the MCT of aluminum with modifying additives.

The excess of the carbon content in the composite after the MCT when compared with its introduced amount is associated with the fact that the modified surface layer of aluminum particles is saturated with a passivating agent (hexane C_6H_{14}) during the MCT. This effect manifests itself most considerably when using stearic acid.

Aluminum is triturated during the MCT. Its particle size distribution both before and after the treatment was determined using a Mastersizer 2000 device (Malvern Instruments, Great Britain). In contrast with the average particle size of the initial powder $d = 50 \mu\text{m}$, that of aluminum treated with 3% C for 20 min decreases to 36.0 μm , while $d = 16.1 \mu\text{m}$ in the case of 3% PVA and $d = 38 \mu\text{m}$ for the MCT with 3% SA. The Al particle size decreases to 15 μm after the MCT, with

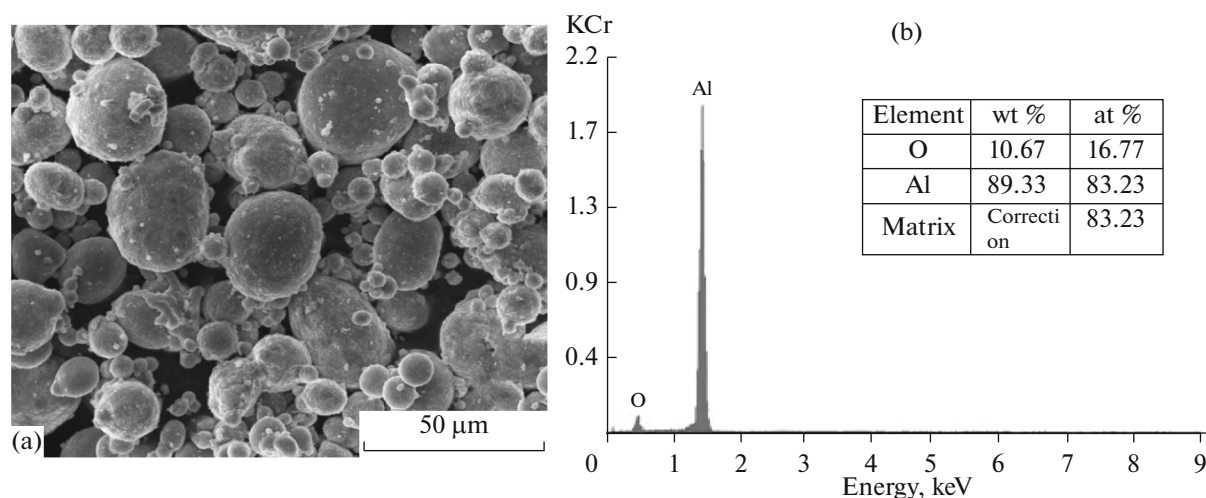


Fig. 1. Characteristics of the initial aluminum powder of the PA-4 grade. (a) Electron microscopy image and (b) weight fraction of elements. Here and below, (b) should be retained (not redrawn).

an increase in the graphite content to 20%, and, correspondingly, the specific powder surface (S_{sp}) measured by the BET method increases (Table 1).

On the contrary, the particle size in the samples treated with PVA and SA increases to 30 and 45 μm , respectively. This is caused by the fact that the particles simultaneously agglomerate and triturate in such cases, causing a decrease in S_{sp} . The obtained formations have a layered structure. However, the specific surface of aluminum particles treated with 20% PVA increases by an order of magnitude, which is associated with the destruction of their agglomerates.

To evaluate the substructural features of aluminum particles after the MCT, we investigated the crystallite sizes (L) by the Scherrer method according to the

Table 1. Specific surface and crystallite size of aluminum after the MCT of Al–modifier composites

Composite composition	S_{sp} , m^2/g	L , \AA
Al _{init}	3.692	560
Al–3% C	4.379	410
Al–5% C	4.843	490
Al–10% C	7.955	540
Al–20% C	9.554	690
Al–3% PVA	4.979	374
Al–5% PVA	1.485	408
Al–10% PVA	1.303	415
Al–20% PVA	14.48	343
Al–3% SA	5.310	500
Al–5% SA	4.371	500
Al–10% SA	3.167	700
Al–20% SA	2.568	700

results of the X-ray phase analysis (XPA) and revealed that they vary during the MCT depending on the type and amount of modifier. The oxide film covering the Al particles is first and foremost destructed during the mechanical trituration of aluminum [18]. Aluminum oxide is crushed in zones of elevated stresses, and its fragments can concentrate in gaps between aluminum particles and along subgrain boundaries or move in the grain bulk in the plastic deformation direction [19]. This phenomenon causes the further crushing of subgrains.

In addition, both the accumulation and redistribution of defects over the particle volume occur during the mechanical effect. The MCT of aluminum with graphite results in crystallite growth with an increase in the carbon content in the Al–C composite. This can be attributed to the fact that carbon atoms penetrate the aluminum particle grain during the MCT and diffuse along with defects over its bulk under the effect of mechanical stresses. It is highly likely that this process promotes the escape of defects on the particle grain boundary and, consequently, the crystallite size rise [20]. The total tendency to a decrease in the size of crystallites of Al particles is observed for the sample treatment with Al–PVA, while an increase is alternatively observed for the MCT with Al–SA with an increase in amount of the modifying additive.

The cause of the crystallite growth can be also the sink of dislocations generated during the mechanical (force) effect on the sample surface into the zones where the Al particle chemically interacts with organic modifier additives and an encapsulating layer protecting the particle against oxidation forms on the aluminum surface.

Spectroscopic analysis methods allow us to understand the interrelation between the elements representing different functional groups, of which the sur-

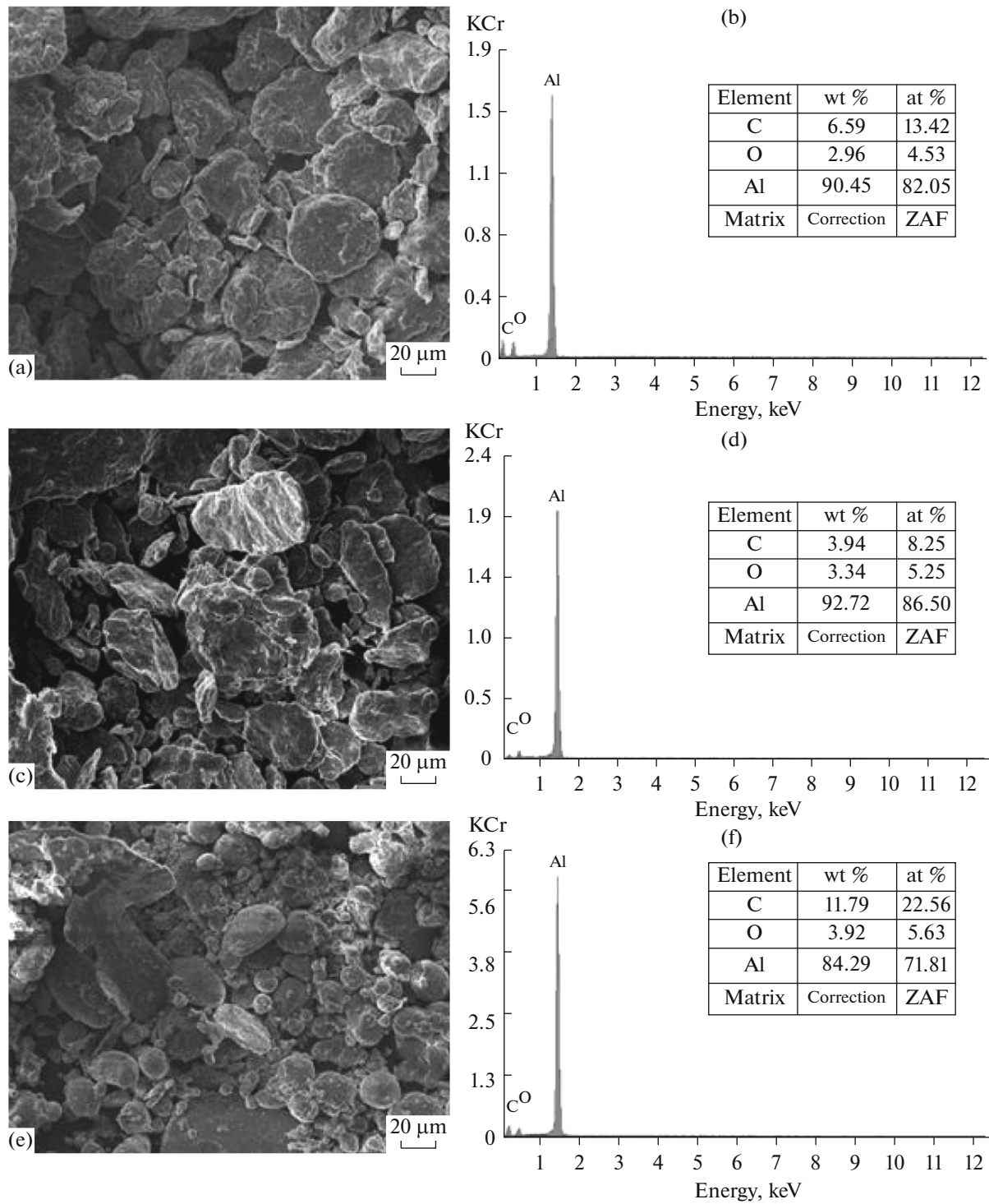


Fig. 2. Structural characteristics of composites after the MCT. (a, b) Al–3% C sample, (c, d) Al–3% (C₂H₃OH)_n sample, and (e, f) Al–3% C₁₇H₃₅COOH. (a, c, e) Electron microscopy images and (b, d, f) energy dispersion spectra and weight fraction of elements.

face structure of material particles is formed. Figure 3 shows the IR spectra of powders under study. Lines of stretched and deformation vibrations of the hydroxyl group –OH in region $\nu = 3400$ and 1600 cm^{-1} are present in IR spectra for aluminum in the initial state

(Fig. 3a). An average signal of deformation vibrations of the $\delta_{as}\text{Al–OH}$ compound is observed at a frequency of 1186 cm^{-1} . Consequently, the surface layer of Al particles contains not only aluminum oxide, but also hydroxide. The intensity of the signal of hydroxyl

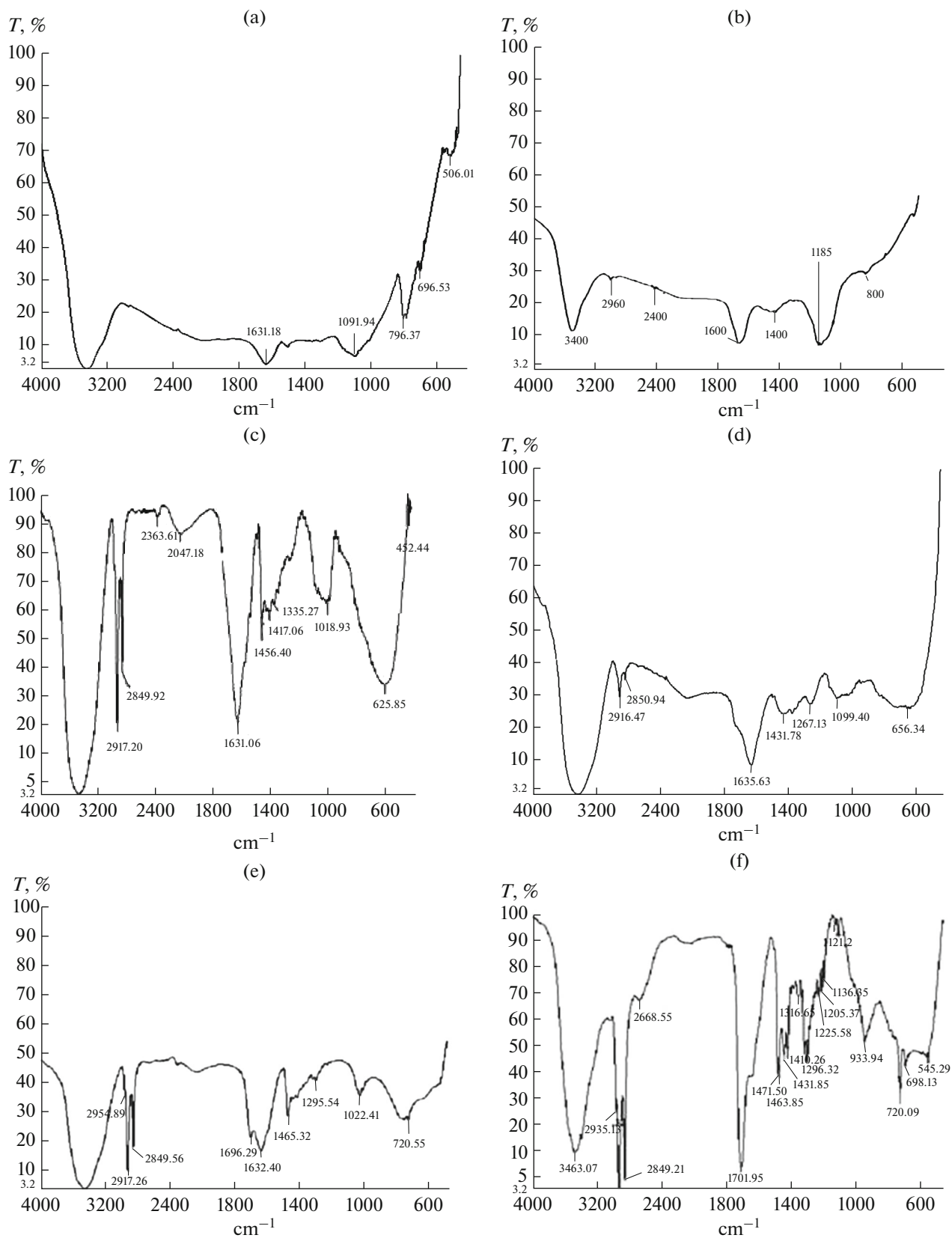


Fig. 3. IR spectra of powders under study—(a) initial and (b–f) after the MCT. (a) Al_{init} , (b) Al-3%C, (c) Al-3% $\text{C}_2\text{H}_3\text{OH}_n$, (d) Al-20% $\text{C}_2\text{H}_3\text{OH}_n$, (e) Al-3% $\text{C}_{17}\text{H}_{35}\text{COOH}$, and (f) Al-20% $\text{C}_{17}\text{H}_{35}\text{COOH}$.

groups –OH after the joint mechanical treatment of aluminum powders with 3% graphite decreases three-fold (Fig. 3b); i.e., the partial removal of hydroxide from the particle surface occurs.

Considerable variations in the IR spectra are observed after the mechanical activation of the Al–PVA sample (Fig. 3c). Absorption bands, referred to vibrations of –CH₃ and –CH₂ groups ($\nu = 2917.20$ and 2849.92 cm^{-1}), and clear bands $\nu(\text{OH})$ of a water molecule (1681 cm^{-1}) and carboxylate ion (1466.40 cm^{-1}), as well as absorption bands of primary, secondary, and tertiary alcohols at $\nu = 1385$ and 1417 cm^{-1} , occur on the surface of aluminum powders.

The intensity of fundamental lines, which were observed in the spectrum of the Al–3%C composite, enhanced considerably. This is especially attributed to the hydroxyl group –OH (3400 cm^{-1}). The MCT of aluminum with polyvinyl alcohol resulted in an intense absorption band at a frequency of 1018.93 cm^{-1} , which is attributed to the Al–O group. These spectra are a result of PVA destruction under the mechanical effect and formation of radical groups on the particle surface.

The intensity of almost all absorption bands, including those of hydroxyl groups, decreases with an increase in the amount of PVA in the Al composite (from 3 to 20%) (Fig. 3d). These changes in the structure of the surface layer are possibly caused by the interaction of PVA with hexane, which provides the additional dispersal of particles and an increase in the specific surface area, which causes a decrease in the amount of organic groups per unit of the newly formed active surface.

Similar structural changes of the surface are also observed for the joint treatment of aluminum with 3% SA (Fig. 3e). Basic surface centers are formed on the broken surfaces of Al particles during the MCT, and clear bands $\nu(\text{OH})$ and $\delta(\text{OH})$ of molecules of the coupled OH group appear at frequencies of 3400 and 1632 cm^{-1} . Strong intense signals of carboxylate ions with vibration types $\nu_{\text{as}}\text{ C–O}$ and $\nu_{\text{s}}\text{ C–O}$ are observed at $\nu = 2954, 2917,$ and 2849 cm^{-1} . Similarly to composition Al–3% PVA, a signal from the Al–O group—but shifted from 1018.93 cm^{-1} to 1022.41 cm^{-1} —is fixed. There are also some low-intense signals on the right slope of the fundamental CH₂ band (the pendulum oscillation) in the range $\nu = 770\text{–}720\text{ cm}^{-1}$.

The intensity of absorption bands from hydroxyl groups, especially at $\nu = 3464$ and 1701 cm^{-1} , increases with an increase in the SA content in the treated system to 20% (Fig. 3f). In addition, we observed numerous signals from stretched asymmetric vibrations of aliphatic –CH₃ groups (2955 cm^{-1}) and stretched symmetric vibrations of aliphatic –CH₂ groups (2849 cm^{-1}). Absorption frequencies of 1346 and 1431 cm^{-1} are attributed to carbonyl groups, and

Table 2. Active aluminum content in the composition of Al–modifier composites after the MCT

Composite composition	$C_{\text{Al}_{\text{act}}}, \%$
Al _{init}	97.70
Al–3% C	96.90
Al–5% C	95.90
Al–10% C	90.35
Al–20% C	88.06
Al–3% PVA	91.00
Al–5% PVA	95.50
Al–10% PVA	86.05
Al–20% PVA	89.05
Al–3% SA	98.90
Al–5% SA	96.75
Al–10% SA	85.80
Al–20% SA	79.95

the band at 1701 cm^{-1} belongs to stretched vibrations of C=O groups. When compared with the sample containing 3% SA, intense bands of low-frequency vibrations of –CH groups are clearly pronounced for the Al–20%SA composite in the range $\nu = 720\text{–}540\text{ cm}^{-1}$. However, the bands of deformation vibrations of Al–O–Al appear instead of Al–O in range $\nu = 990\text{–}715\text{ cm}^{-1}$. The MCT of the Al–20%SA sample increases the signal intensity of almost all groups, including –OH, –CH₂, CH₃, –C–O, and –C=O.

Thus, the results of IR spectroscopy of mechanochemically treated and modified aluminum powder showed that considerable changes in the structure of the surface layer of Al particles occur during the MCT. Several types of active centers, which are able to enter chemical reactions when using these compositions in the composition of various combustible mixtures, are formed during the mechanical activation of aluminum with organic additives. It is shown by the example of the Al–SA composite that the intensity of absorption bands from various groups considerably increases with an increase in amount of the modifier in its composition, which evidences an increase in the thickness of the organic layer on the particle surface.

The active aluminum content ($C_{\text{Al}_{\text{act}}}$) in the composition of powder triturated in a mechanical reactor and modified with organic additives was evaluated using the volumetric method by the liberation of hydrogen during the interaction of aluminum with 20% aqueous sodium hydroxide solution [21]. The solid product of the reaction is pseudoboehmite AlOOH.

The content of active aluminum in compositions under study with various modifiers varies in the limits of 79.95–96.9% (Table 2). Herewith, we should take into account that the weight fraction of aluminum in

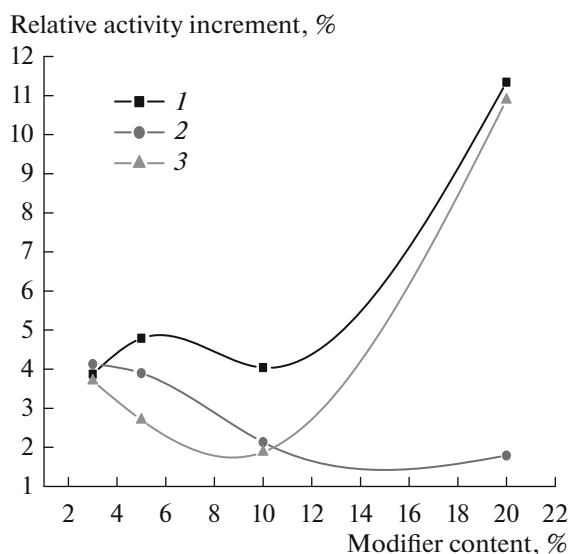


Fig. 4. Relative index of the increment of active aluminum in composites (1) Al–C, (2) Al–SA, and (3) Al–PVA after the MCT.

mixtures under study decreases from 5 to 20%; i.e., an increase in the active aluminum content in the composite with respect to initial aluminum takes place in all cases. This is primarily caused by the fact that the oxide film on the Al particle surface is partially reduced by a carbon modifier during the MCT, and the active aluminum content in the composite increases due to this process.

The absence of a stable regularity in the variation in the active aluminum content in the composite depending on the modifying additive content during PVA and SA treatment can be associated with the formation of the organic encapsulating film on the particle surface.

The relative index of the active aluminum increment in the Al–modifier composite can be evaluated according to the formula [22]

$$\Delta J = J_x - \frac{J_0 \omega_{Al}}{100},$$

where J_x and J_0 are experimental active aluminum contents in the Al–modifier composite and initial aluminum powder, respectively, %; and ω_{Al} is the weight fraction of aluminum in the Al–modifier composite, %.

Figure 4 shows the dependence of the relative increment of the aluminum activity after the MCT of the Al–modifier mixture on the organic additive content in it. The best result (11.34%) was observed to the Al–20% C composite.

Relatively high index $\Delta J = 10.89\%$ is also observed in the Al–20% PVA composite, while it was only 1.79% for the Al–20% SA sample. The largest increment in the aluminum activity during the MCT of alu-

minum with SA is fixed only for a content no higher than 3%.

It follows from our data that the aluminum activity increases with an increase in the carbon and PVA content in the Al composite. However, its increase in the case of SA additive lowers this index, which can be associated with the fact that a dense encapsulating layer poorly soluble with alkali is formed on the surface of aluminum particle during the trituration of the Al–SA mixture with a large SA amount (more than 5%).

CONCLUSIONS

Thus, a complex analysis of activated and modified aluminum powders showed that the particle surface is saturated by solid solutions of carbon-containing compounds during the MCT. The modification of the surface makes it possible to exclude the defect sink from the particle bulk on its surface, i.e., to fix an active state of metallic particles and energy intensity of the system in general.

The use of such powder materials is efficient, in particular, when fabricating SHS composites with increased chemical activity [16, 17] and for various energy-intensive systems of various applications (explosives and solid rocket fuels).

REFERENCES

1. Heinicke, G., *Tribochemistry*, Berlin: Akademie, 1984.
2. Mansurov Z.A. and Mofa N.N., *Mekhanokhimicheskii sintez kompozitsionnykh materialov* (Mechanochemical Synthesis of Composite Materials), Almaty: Kazakh Univ., 2016.
3. Avvakumov, E.G., *Mekhanokhimicheskie metody aktivatsii khimicheskix proceccov* (Mechanochemical Activation Methods of Chemical Processes), Novosibirsk: Nauka, 1986.
4. Zhang, D.L., Processing of advanced materials using high-energy mechanical milling, *Progr. Mater. Sci.*, 2004, vol. 49, pp. 537–560.
5. Koch C.C. and Whittenberger J.D., Mechanical milling. Alloying of intermetallics, *Intermetallics*, 1996, vol. 4, no. 5, pp. 339–355.
6. Suryanarayana, C., Mechanical alloying and milling, *Progr. Mater. Sci.*, 2001, vol. 46, nos. 1–2, pp. 1–184.
7. Gaffet, E., Bernard, F., Nierce, J.-C., Charlot, F., Gras, C., and Le Caer G., Some recent developments in mechanical activation and mechanochemistry, *J. Mater. Chem.*, 1999, vol. 9, pp. 305–314.
8. Butyagin, P.Yu., Problems and prospects of the development of mechanochemistry, *Usp. Khim.*, 1994, vol. 63, no. 12, pp. 1031–1043.
9. Avvakumov, E., Senna, M., and Kosova, N., *Soft Mechanochemical Synthesis: A Basics for New Chemical Technologies*, Boston–Dordrecht–London: Kluwer, 2001.
10. Balaz, P., *Mechanochemistry in Nano Science and Mineral Engineering*, Springer, 2008.

11. Fman, S. and Toas, J., Mechanoluminescence of quartz particles in stirred media mill, *Fourth International Conference on Mechanochemistry and Mechanical Alloying*, Braunschweig, Germany, 2003, pp. 56–57.
12. Dossi, S., Paravan, C., Maggi, F., and Galfetti, L., *Enhancing micrometric aluminum reactivity by mechanical activation*, *AIAA*, 2015, pp. 4206–4221.
13. Streletskii, A.H., Kolbanov, K.V., Troshin, K.Ya., Borisov, A.A., Leonov, A.V., Mudretsov, S.N., Artemov, V.V., and Dolgoborodov, A.Yu., Structure and reactivity of mechanically activated Mg(Al) MoO₃ nanocomposites, *Khim. Fiz.*, 2016, vol. 35, no. 7, pp. 79–91.
14. Streletskii, A.N., Kolbanov, I.V., Borunova, A.B., and Butyagin, P.Yu., Mechanical activation of aluminum. 3. Kinetics of the interaction of aluminum with water, *Kolloidn. Zh.*, 2005, vol. 67, no. 5, pp. 694–701.
15. Dolgoborodov, A.Yu., Streletskii, A.H., Makhov, M.N., Kolbanov, K.V., and Fortov, V.E., Explosive compositions based on mechanically activated metal-oxide mixtures, *Khim. Fiz.*, 2007, vol. 26, no. 12, pp. 40–45.
16. Sadykov, B., Sabayev, Zh., Bakkara, A., Deluca, L., Mofa, N., and Mansurov, Z., SH-synthesis of aluminosilicate ceramics: mechanochemical activation and regularities of combustion, *Sci. Res. Abstr. Appl. Miner. Adv. Mater.*, 2015, vol. 4, p. 49.
17. Mofa, N.N., Sadykov, B.C., Bakkara, A.E., and Mansurov, Z.A., Combustion features of energetic condensed systems with mechanically activated metallized composites, in: *Tr. 7-i Mezhdunarodnoi konferentsii SPACE'2015 "Kosmicheckii vyzov XXI veka"* (Proc. 7th Int. Conf. SPACE'2015 "Space Challenge of the XXI Century"), Sevastopol', 2015, pp. 61–63.
18. De Luca, L.T., Galfetti, L., Colombo, G., Maggi, F., Paravan, C., Reina, A., Dossi, S., Fassina, M., and Sossi A., *Metal Nanopowders: Production, Characterization, and Energetic Applications*, Weinheim: Wiley, 2014.
19. Kirichenko, O.A., Ushakov, V.A., Andryushkova, O.A., Ivchenko, S.V., and Poluboyarinov V.A., Phase transformations and mass transfer in mechanically activated low-temperature aluminum oxides, *Neorgan. Mater.*, 1999, vol. 15, no. 5, pp. 333–341.
20. Avakumova, E.G., *Fundamental'nye osnovy mekhanicheskoi aktivatsii, mekhanosinteza i mekhanokhimicheskikh tekhnologii* (Fundamentals of Mechanical Activation, Mechanochemical Synthesis, and Mechanochemical Technologies), Novosibirsk: Nauka, 2009.
21. *GOST (State Standard) 9454–95: Aluminum Powder. Technical Specifications*, Minsk, 1997.
22. Bakkara, A.E. Effect of additives of metal nanoparticles on combustion of condensed systems, *Extended abstract of Doctoral (Ph.) Dissertation*, Almaty: al-Farabi Kaz. Nats. Univ., 2017.

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