

HYDROTHERMAL OXIDATION OF ALUMINUM FOR HYDROGEN AND ALUMINUM OXIDE/HYDROXIDE PRODUCTION

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Abstract

Aluminum-water reaction is carried out in special reactor developed for continuous and large-scale production. Reaction proceeds under about 300 °C and 15 MPa. The products of this reaction are monophasic aluminum oxyhydroxide (gamma-AlOOH) and hydrogen. Hydrogen produced within the reactor due to aluminum-water reaction is transferred to the fuel cell or accumulated in hydrogen tanks. Produced gamma-AlOOH represents the powder consisting of agglomerated particles with the size of about 10 μm, the size of single crystal ranges from about 10 to 200 nm, specific surface from 30 to 110 m²/g.

Key words: aluminum, energy, hydrogen, boehmite, hydrothermal oxidation, surface morphology, crystal size, surface area, pore structure, phase composition

1. INTRODUCTION

One of perspective future energy carriers is hydrogen. It can be produced from water through electrolysis that means that the potential reserve of hydrogen on the Earth is practically unlimited. Hydrogen is environmentally friendly in terms of that the process of its combustion is less polluting than that of fossil fuels, so the use of hydrogen for energy production decreases the charges for eco-activity. However, in spite of the fact that hydrogen energy has been under research for several decades up to now and for this time it has changed into individual scientific area (Vanderryn et al., 1977), the hydrogen still hasn't obtained the recognition of energy market mainly due to storage and transportation problems (Zhou, 2005, Ross, 2006), which are still open as decades ago.

Since hydrogen energy problems are still not solved, the attention is called by other non-organic energy carriers. One of these perspective energy carriers is aluminum (Shkolnikov et al., 2011). Unlike hydrogen, aluminum is easy to transport and store. When metal is placed into the atmosphere, it is covered by oxide film, which protects metal from further corrosion, thus providing the safety of its storage and transportation. Like hydrogen, aluminum is renewable. It has high calorific value and high concentration in the earth's crust.

Chemical energy stored in aluminum can be converted into useful electrical or thermal energy by two different methods: by direct anodic oxidation or through chemical oxidation and following conversion of produced hydrogen and heat into electrical energy. Special attention in aluminum-based energy technologies is given to activation techniques which improve the reaction kinetics. Aluminum is covered by oxide film that should be damaged when aluminum oxidizes within power plant. It is possible to develop different type aluminum-fueled power plants from several watts to mega watts and cover portable, transport and stationary applications.

Exothermic process of aluminum oxidation in aqueous solutions with the production of hydrogen as intermediate fuel is one of the effective technologies that convert aluminum chemical energy into useful energy (electrical or thermal) (Zhuk et al., 2006, Mahmoodi and Alinejad, 2010, Franzoni et al., 2010, Kolbenev, 1993, Martínez et al., 2005, Miller et al., 2002). Aluminum oxidation in water and aqueous solutions has been given considerable attention for the last decades. An interest in this process is due to the high chemical activity of highly dispersed (micrometer size) aluminum powders in the reactions with water and water vapor. The use of pure water as an oxidant in its reaction with dispersed aluminum makes it possible to synthesize high purity hydrogen, a large amount of high-

temperature steam (Vlaskin et al., 2010), and a variety of aluminum hydroxides. The main element of the units for hydrothermal oxidation of aluminum by water or steam is a reactor that generates a steam–hydrogen mixture, which can be used as a working medium of conventional and future heat engines and generators.

Hydrothermal oxidation of aluminum is the process producing not only hydrogen and/or energy but also a variety of alumina-based materials. Economic of this process now can be based on all products of the process. The process of aluminum oxidation in water can be used directly for hydrogen and heat production in energy applications, while the solid products of aluminum oxidation can be sent to aluminum recycling or obtaining the advanced aluminas. Advanced aluminas are used today in a wide spectrum of non-metallurgical applications including ceramics, adsorption, catalysis, active substance carrying etc.

Present work gives the description principle and operation features of aluminum-fueled power plants based on hydrothermal oxidation of aluminum. Paper presents the results of the investigation of physicochemical properties of solid product produced by hydrothermal oxidation of aluminum micron powder in experimental flow reactor. The comparison of the results of the investigation of oxidation product structure with the results of kinetics study is also described to examine the reaction mechanism.

2. REACTOR OF HYDROTHERMAL OXIDATION OF ALUMINUM

Schematic view of the reactor of hydrothermal oxidation of aluminum is shown on Fig. 1. Figure illustrates the supply of reagents into the reactor and the exit of products. Aqueous suspension of aluminum powder is supplied from top through nozzles using a dosing pump. The outlet of gaseous products is in the upper part of the reactor and the bottom has the outlet for the solid and liquid phases.

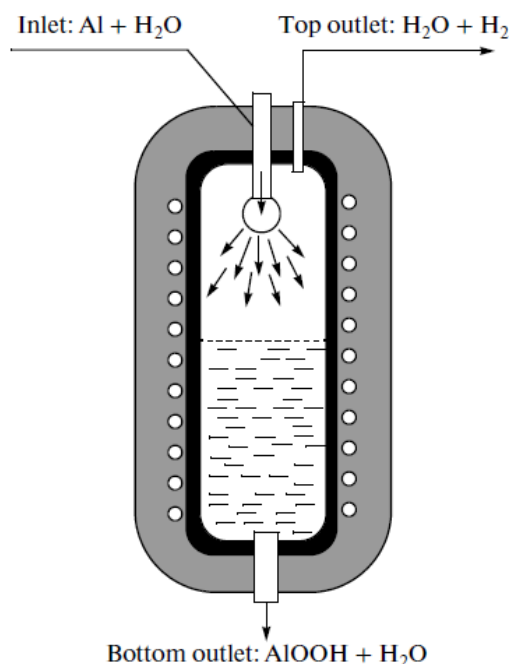


Fig. 1. Schematic view of the reactor of hydrothermal oxidation of aluminum.

Reactor represents the elongated cylinder with length of 1.9 m. Reactor volume is 7570 cm³. On reactor external surface the 5 kW ohmic heater is installed. Reactor is heat-insulated. Initial reagents (aluminum and water) enter into the reactor with the help of high-pressure plunger pump. Aluminum powder enters into the reactor in the form of aluminum-water mixture, which is preliminary prepared in mixing tank. Reaction products are removed from the reactor into the oxidation products receiving

tank. Experimental plant is equipped by cutoff valves, thermocouples installed on reactor external surface and pressure detectors. Experimental plant is managed from remote operating room by means of computer-based control system. Indications of all sensors are written on hard disk drive of the computer.

Reactor of hydrothermal oxidation of aluminum is loaded by aluminum micron powder (with average particle size up to 70 μm) as primary fuel and water as primary oxidant. Deionized water is usually used. The purity of aluminum is 99.88 %.

3. KINETICS OF ALUMINUM OXIDATION

3.1 Calculation of activation energy

Kinetic curves $\alpha(t)$ for heterogeneous chemical reactions generally obey a logarithmic law:

$$\alpha(t) = \text{const}_1 + \text{const}_2 \times \ln t. \quad (1)$$

Chemical reaction rate $W = d\alpha/dt$ is proportional to the reaction rate constant K , which for heterogeneous chemical reactions also depends on the stage of the reaction:

$$K = K_0 \times \exp\left(-\frac{E_a}{RT}\right), \quad (2)$$

where K_0 - pre-exponential factor, E_a - the activation energy, and R - the universal gas constant (8.31 J/moleK). In general, the distribution of the rate constants of these stages is due to differences in pre-exponential factors and activation energies. Temperature dependence of the characteristic time for each step of the heterogeneous reaction in $\ln(1/T)$ coordinates is a straight line with the slope which is the ratio of activation energy to the universal gas constant:

$$\ln t = \text{const} + \frac{E_a}{R} \times \frac{1}{T}. \quad (3)$$

By equation (3) the estimation of activation energy from the data obtained in experiments was carried out.

3.2 Results of kinetic experiments

The synthesis of boehmite at different temperatures was performed during the series of experiments. In each experiment the mixture of aluminum powder with water was prepared at room temperature within mixing tank. Then portion of mixture containing about 50 g of Al was injected by high-pressure dosage pump into preliminary heated 7.5 l reactor. After about 6-14 minutes (depending on reaction rate) the mixture of produced boehmite and water was withdrawn from the reactor. Temperatures at which the synthesis of boehmite was carried out as well as the results of kinetics are presented in Fig 2.

Reaction time decreases with both initial temperature increasing and powder size decreasing. Particularly for ASD-6 with 0.49 m^2/g specific surface the reaction time decreased from 870 sec at 237 $^{\circ}\text{C}$ to 33 sec at 359 $^{\circ}\text{C}$, for ASD-4 with 0.32 m^2/g specific surface it decreased from 800 sec at 273 $^{\circ}\text{C}$ to 41 sec at 355 $^{\circ}\text{C}$, and for ASD-1 with 0.1 m^2/g specific surface it decreased from 780 sec at 286 $^{\circ}\text{C}$ to 66 sec at 350 $^{\circ}\text{C}$. Aluminum powder ASD-6 was fully oxidized at steam temperatures above 296 $^{\circ}\text{C}$, ASD-4 – above 308 $^{\circ}\text{C}$ and ASD-1 – above 350 $^{\circ}\text{C}$. ASD-6 conversion degree at 237 $^{\circ}\text{C}$ after 14.5 min staying within the reactor was 88 %, ASD-4 conversion degree at 273 $^{\circ}\text{C}$ after 13.3 min staying within the reactor – 74 % and ASD-1 conversion degree at 286 $^{\circ}\text{C}$ after 13 min staying within the reactor – 42 %.

Fig. 3 shows the dependence on temperature in the coordinates $\ln t - 1/T$. With the help of equation (3) from the slope of line that approximates the set of points the values of activation energies E_a were

determined. The values of activation energies are presented in Table. 1. These values were calculated on the assumption that between the induction period and the step of reaction finishing there is only one active step of chemical reaction. Activation energy for oxidation reaction in hydrothermal reactor for aluminum powder with $0.49 \text{ m}^2/\text{g}$ specific surface (ASD-6) was 77 kJ/mole . With powder size increasing the activation energy also increases. For aluminum powder with $0.32 \text{ m}^2/\text{g}$ specific surface (ASD-4) the activation energy was 107 kJ/mole and for aluminum powder with $0.1 \text{ m}^2/\text{g}$ specific surface (ASD-1) the activation energy was 120 kJ/mole .

By mathematical methods from the results presented in Fig. 3 the dependence of t on $1/T$ was established. The coefficients of this dependence are as follows:

$$t = C_1 \times \exp\left(\frac{C_2}{T}\right),$$

- for ASD-6 $C_1 = 10^{-5}$, $C_2 = 9.2 \times 10^3$;
- for ASD-4 $C_1 = 4 \times 10^{-8}$, $C_2 = 12.9 \times 10^3$;
- for ASD-1 $C_1 = 5 \times 10^{-9}$, $C_2 = 14.4 \times 10^3$.

Empirically established coefficients in equation (4) have been used in the future when calculating the reactor volume required for its continuous operation. For each powder dispersion the value of time t obtained from equation (4) for specific aluminum powder gives minimum necessary (for close to 100 % oxidation conversion) time of passing of aluminum particle through the reactor.

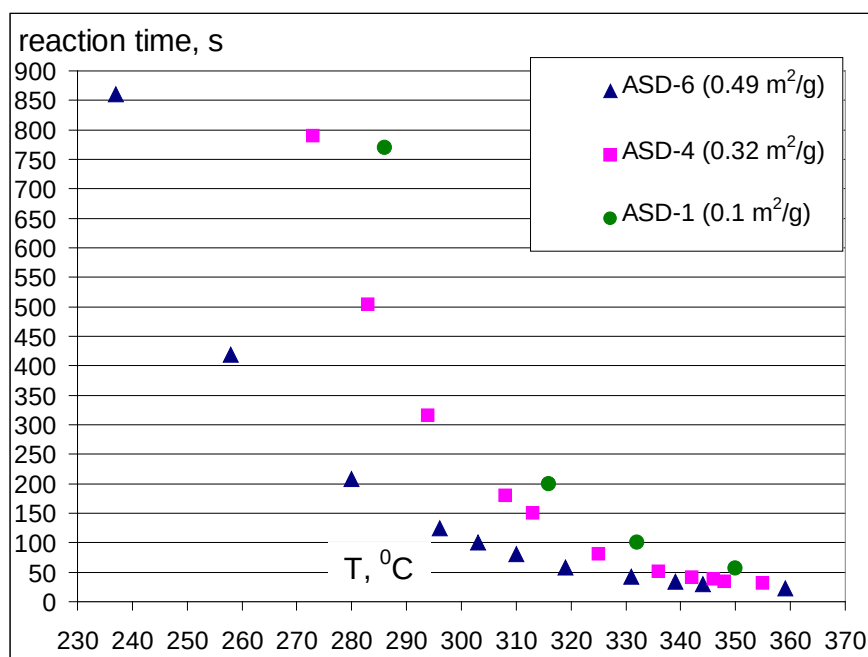


Fig. 2. Reaction time depending on reactor temperature and powder dispersion.

4. ALUMINUM OXIDATION SOLID PRODUCT

SEM images of solid oxidation products synthesized from aluminum powder ASD-6 with $0.49 \text{ m}^2/\text{g}$ specific surface at different temperatures are shown in Fig. 4. SEM images demonstrate that the structure of product becomes more externally ordered with temperature decreasing. With temperature increasing the smooth form of product is lost due to the increasing of particle agglomeration.

Fig. 4 shows SEM images of solid oxidation product synthesized from aluminum powder ASD-6 with $0.49 \text{ m}^2/\text{g}$ specific surface at one temperature. It is the same product as in Fig. 4a but in Fig. 5 it is

presented at larger magnifications. From the series of such images it was established that oxidation products represent agglomerates and consist of crystals with the size of 10-200 nm. So, these images indicate the microporous structure of the product. From SEM analysis it was also observed that with temperature decreasing the average size of crystals on the surface of product decreases (Fig. 6). It can be explained simply by the fact that crystal grows faster at high temperatures because a number of collisions between growing crystal and crystal nucleus per unit of time increases.

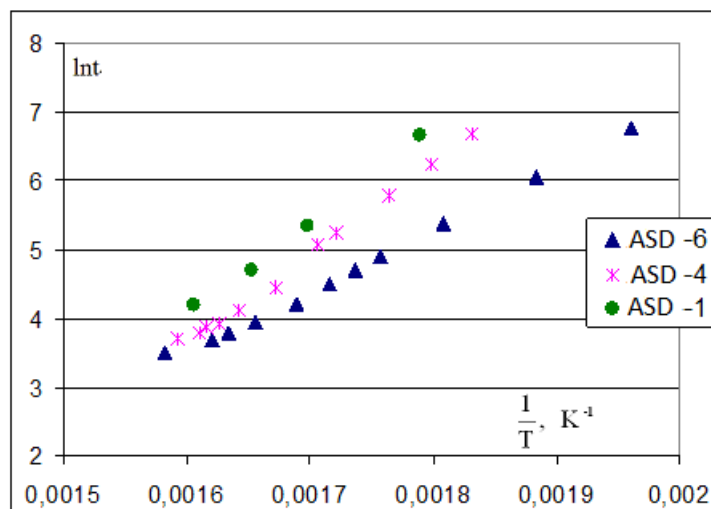


Fig. 3. $\ln t - 1/T$ dependence.

Table. 1. Values of activation energies E_A for aluminum oxidation reaction in hydrothermal reactor for aluminum powders with different dispersion.

Aluminum powder	Specific surface, m^2/g	E_A , kJ/mole
ASD-6	0.49	77
ASD -4	0.32	107
ASD -1	0.1	120

Specific surface of solid product depending on synthesis temperature is shown in Fig. 7. BET analysis showed that temperature increasing leads to the decreasing of specific surface of synthesized product. Specific surface decreased from $110 m^2/g$ at $237^\circ C$ to $38 m^2/g$ at $359^\circ C$ that confirms the results of microscopic study (specific surface decreases with average crystal size increasing). The results of analysis of structural properties of boehmite confirmed that hydrothermal oxidation of aluminum is a promising method of the production of advanced aluminas. High surface area allow considering the product of hydrothermal oxidation of aluminum as perspective catalyst carrier or sorbent. An additional advantage of this method is the possibility to assign the structural properties of nanocrystalline product by thermodynamic parameters within the reactor.

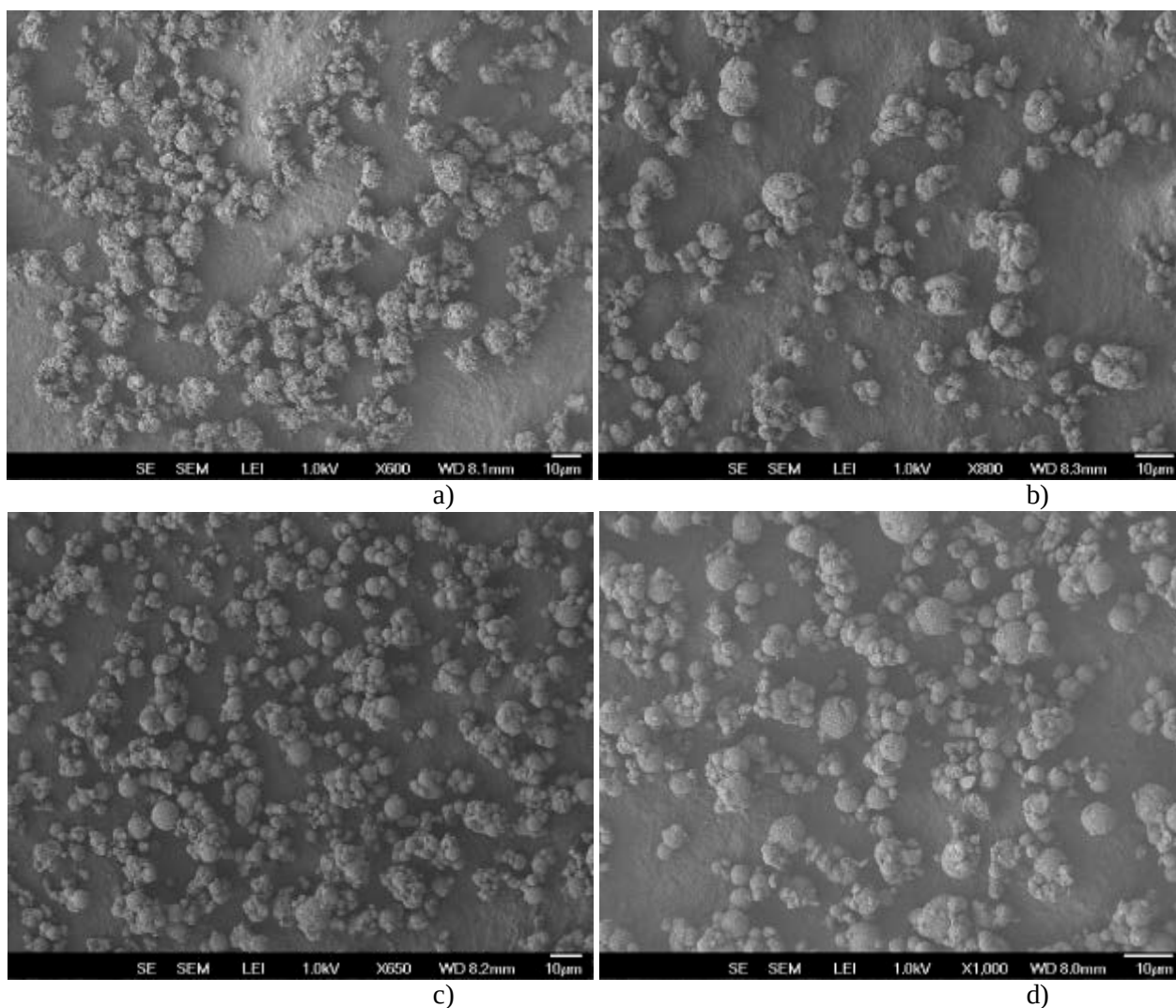


Fig. 4. SEM images of solid oxidation products synthesized at different temperatures (°C): a) 339, b) 303, c) 280, d) 258

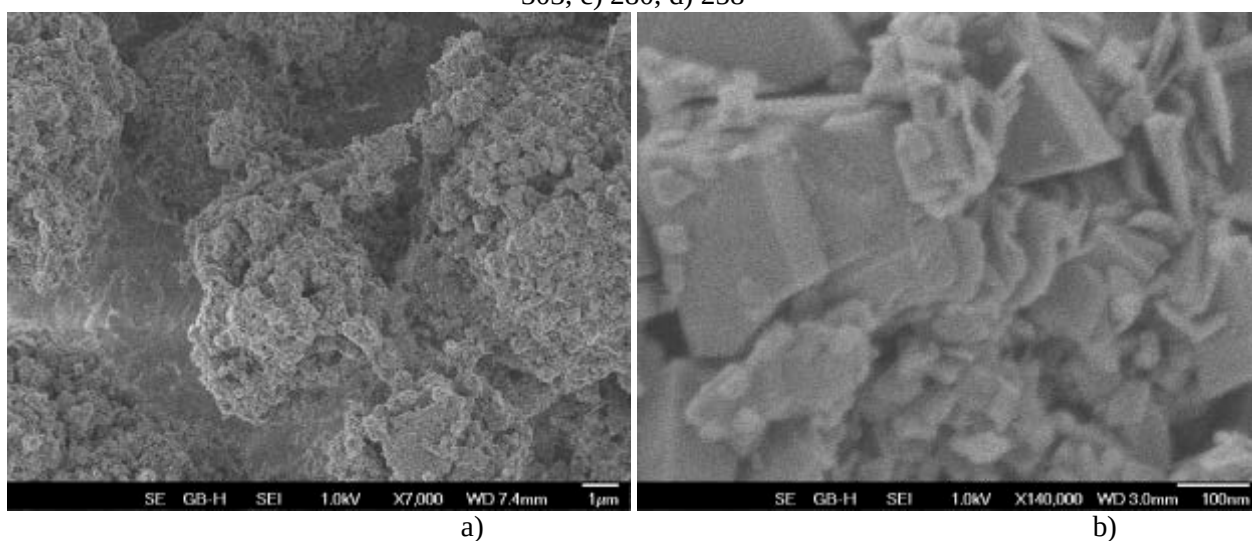


Fig. 5. SEM images of solid oxidation product synthesized at 339 °C at different magnifications: a) 7000, b) 140000

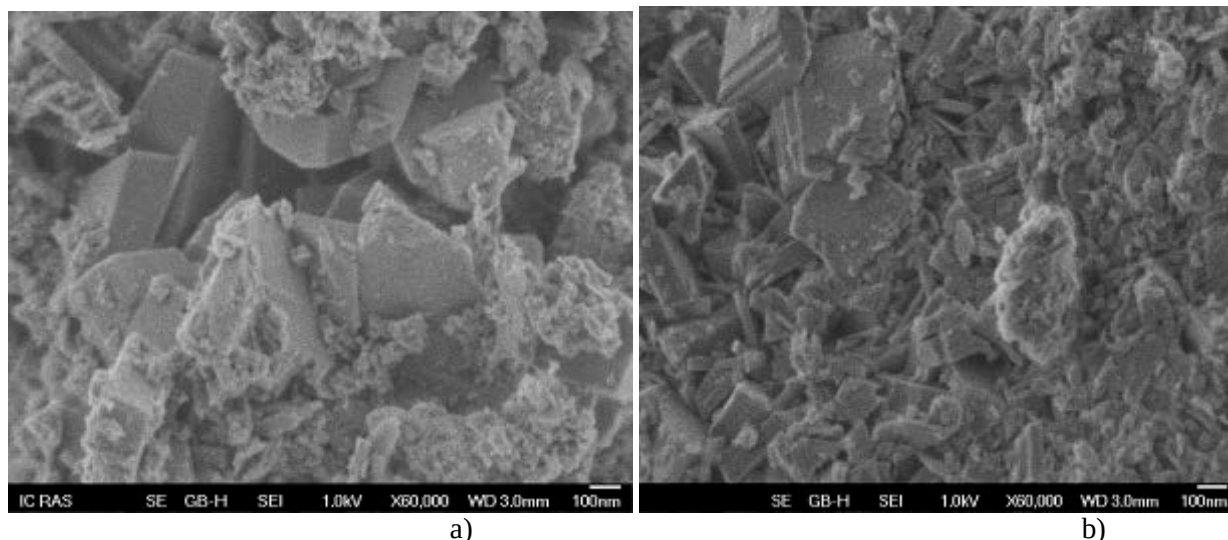


Fig. 6. SEM images of crystals on the surface of product synthesized at different temperatures (°C): a) 359, b) 280

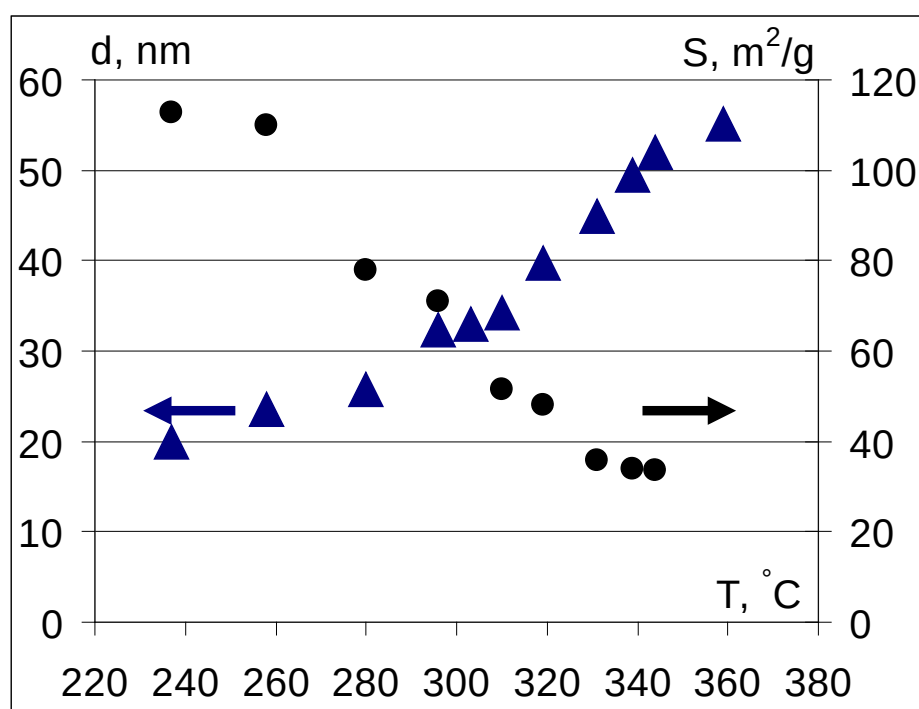


Fig. 7. Average size of boehmite crystals (d , nm) and specific surface of solid product (S , m^2/g) depending on temperature

5. ALUMINUM-FUELED ENERGY TECHNOLOGICAL PLANTS

5.1 Experimental co-generation power plant with $10 \text{ nm}^3/\text{hour}$ hydrogen production

Energy-effective and multi-purpose technology of hydrothermal aluminum oxidation was firstly realized in experimental co-generation power plant CGPP-10 intended, first of all, for autonomous energy supply. The view of this plant is shown on Fig. 8. For the first time the power plant utilizes aluminum as a fuel. CGPP-10 works in non-stop autonomous regime not depending on external grid. It produces hydrogen, electrical and thermal energy, as well as nanostructured powder of aluminum

hydroxide. Technical characteristics of experimental co-generation power plant CGPP-10 are shown in table 2. Net power of CGPP-10 is about 10 kW, electrical efficiency and total efficiency regarding to combustion heat of aluminum are 14 % and 72 % respectively. Plant consists from reactor block, fan heater, hydrogen tanks, 16 kW fuel cell battery, inverter and automated control system. Power plant can produce as final products both electrical energy and hydrogen with 10 nm³/hour hydrogen production rate. It is important that hydrogen is produced at already high pressure without additional devices and energy inputs on its compression due to high pressure in chemical reactor. Electrical energy produced by fuel cell in direct current is converted into three-phase current and supplied to power plant auxiliary thus making its autonomous working.

5.2 Energotechnological complex with 100 nm³/hour hydrogen production

The technology of hydrothermal aluminum oxidation with the production of marketable products (AlOOH and H₂), electrical and thermal energy was realized in experimental energotechnological complex ETC-100, which produces marketable products: nanocrystalline aluminum hydroxide, hydrogen, as well as electrical and thermal energy. Nanostructured aluminum hydroxide, which is produced by plant in industrial scale, is market-desired product, which is purchased today from abroad. The view of energotechnological complex ETC-100 is shown in fig. 9. Main technical characteristics of energotechnological complex ETC-100 are shown in table 3.



Fig. 8. The view of experimental co-generation power plant CGPP-10 for autonomous energy supply.

Table 2. Technical characteristics of experimental co-generation power plant CGPP-10.

Parameter	Value
Aluminum consumption rate, kg/hour	9.4
Aluminum hydroxide (boehmite) production rate, kg/hour	19
Thermal power, kW	40
Hydrogen production, nm ³ /hour	10
Auxiliary, kW	4
Electrical power, kW	10.6
Electrical efficiency, %	14
Total efficiency, %	72



Fig. 9. The view of energotechnological complex ETC-100.

Table 3. Technical characteristics of energotechnological complex ETC-100.

Parameter	Value
Aluminum consumption rate, kg/hour	101
Water consumption rate at the input to the water-preparatory device, kg/hour	484
Average reactor temperature, °C	324
Average reactor pressure, MPa	150
Auxiliary, kW	28
Hydrogen production, nm ³ /hour	110
Thermal power, kW	260
Aluminum hydroxide (boehmite) production rate, kg/hour	203

6. CONCLUSIONS

Aluminum-water reaction was carried out in special reactor developed for continuous and large-scale production. Reaction proceeds under about 300 °C and 15 MPa. The products of this reaction are monophase aluminum oxyhydroxide (gamma-AlOOH) and hydrogen. Hydrogen produced within the reactor due to aluminum-water reaction is transferred to the fuel cell or accumulated in hydrogen tanks. Produced gamma-AlOOH represents the powder consisting of agglomerated particles with the size of about 10 μm, the size of single crystal ranges from about 10 to 200 nm, specific surface from 30 to 110 m²/g. The results of analysis of structural properties of boehmite confirmed that hydrothermal oxidation of aluminum is a promising method of the production of advanced aluminas. High surface area allow considering the product of hydrothermal oxidation of aluminum as perspective catalyst carrier or sorbent. An additional advantage of this method is the possibility to assign the structural properties of nanocrystalline product by thermodynamic parameters within the reactor. Two energotechnological plants were created: experimental co-generation power plant CGPP-10 with 10 nm³/hour hydrogen production rate and energotechnological complex ETC-100 with 100 nm³/hour hydrogen production rate. The description principle and operation features of these aluminum-fueled power plants based on hydrothermal oxidation of aluminum have been described.

Aluminum-fueled power plants are developed mainly for clean-energy generation. It is supposed that such power plants are appropriate for eco-tensity regions, e. g. for megapolises. They can be successfully applied as emergency, on-peak power and standby plants. There are also a number of military applications. For example, aluminum-water propulsion is favourable for submarine or ship

energy supply, because in this case seagoing craft takes on its board only fuel (aluminum), while oxidizer (water) is supplied from the outside. So, aluminum as a fuel might be used in a number of special energy applications, thus contributing to energy system.

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