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APPLICATION OF ALUMINUM NANOPOWDER IN HYDROGEN POWER ENGINEERING

A.P. Ilyin, A.V. Korshunov, L.O. Tolbanova

Tomsk Polytechnic University
E-mail: tolbanowa@tpu.ru

The results of researches on interaction of aluminum nanopowder with water have been given. It is shown, that in conditions of relatively low temperatures aluminum nanopowder totally cooperates with water, allocating «hot» hydrogen. The interaction process is accompanied by the chemical-mechanical effect, decrease of water boiling temperature and self-heating of reacting particles. The formed nanoporous materials have various chemical and phase structure. Advantages and disadvantages of aluminum nanopowder application for obtaining hydrogen are analyzed.

1. Urgent problems of earth energy

Existence of terrestrial civilization is directly connected with kinds of energy sources which will be used by mankind. One of today problems is a search for new energy sources which could replace in the near future oil, gas and coal the resources of which are depleted in the nearest hundred years by specialists estimation. Undoubtedly, that in the nearest hundred years the nuclear power engineering is developed intensively along with unconventional power sources (wind-power engineering, tidal power stations, geothermal stations etc.). Intensive development of nuclear power engineering puts sharply the problem of radioactive waste disposal. Unfortunately, radioactivity of wastes from nuclear station operation is hundred times higher than of original fuel; and waste disposal on Earth results in significant growth of radiation background that may result in abrupt growth of population morbidity. One of the perspective projects of waste disposal is their transportation from Earth by spacecrafts in the direction of the Sun. Certainly, at present such project requires great investments that make nuclear power engineering unprofitable. By specialists predictions the controlled thermonuclear fusion is realizable in 100...200 years. Probably, powerful sources of electric energy will be developed but the problem of creating mobile energy sources, for example, for automobiles, remains.

2. Perspectives and problems of hydrogen power engineering

The most perspective direction among the known technologies of obtaining and transporting energy is the hydrogen power engineering (HPE). HPE and hydrogen are characterized by the following features [1]:

- there is much hydrogen in nature – it is water, H_2 content amounts to составляет 17 at. % on Earth;
- H_2 is the lightest element therefore, it has the highest energy intensity per mass unit – 121 MJ/kg;
- oxidation (combustion) product of H_2 is H_2O – ecologically the safest product;
- in the case of H_2 leakage at its use in huge bulks it is not accumulated in Earth atmosphere: H_2 light molecules «accelerate» to orbital velocity as a result of collision with air molecules and fly out of earth gravity;
- fuel elements in which electric energy is produced using H_2 and O_2 of air with efficiency ≈80 % are developed.

At the same time, the perspectives of HPE scale use are not so unclouded; there is a number of problems as in any technology:

- problems in H_2 accumulation and storage – this gas forms explosive mixtures with air, it is combustible;
- it is condensed at very low temperature –253 °C, therefore its storage in liquid state is very unprofitable: it should be cooled with liquid helium;
- H_2 storage under the high pressure is complicated that is connected with high penetrability of its molecules.

The idea of obtaining H_2 in solid state under high pressure at cooling is very attractive. The Institute of high-pressure physics is engaged in this problem for a long time (more than 40 years). Solid H_2 is planned to be obtained cooling gaseous H_2, being under pressure $2{\cdot}10^8$ kPa. Characteristics of such H_2: density – to 2000 kg/m^3, stability – to 200 °C are theoretically calculated. Unfortunately, experimental works have not been crowned with success so far. Obtaining solid H_2 could solve many problems of HPE, rocket production and organic synthesis.

3. The unique properties of nanoaluminum

It is known that active metals (Mg, Be and Al) are the carriers of stored chemical energy which may be extracted at combustion. At the same time at interaction with H_2O and water solutions many metals are oxidized by protons and give H_2:

$$Mg+2H^+ \rightarrow Mg^{2+}+H_2\uparrow$$

$$Al+3H^+ \rightarrow Al^{3+}+3/2H_2\uparrow.$$

Molar mass of Mg amounts to 24 g/mole, 24 g of Mg is consumed for obtaining 22,4 l of H_2 at its oxidation. At oxidation of 27 g of Al in H_2O 33,6 l of H_2 is formed that is in 1,5 times more. Al powders produced by industry interacts slowly with H_2O and react only on 20...30 wt. %, and then the process slows down. For a long time a group of ural scientists attempted to accelerate the process introducing Ga, In, rare-earth elements etc. into Al but there was no serious success.

Qualitative leap occurred in the middle of 1980-s when the program on development of electroblasting technology of obtaining superdispersed (nano-) powders (NP) was accepted in USSR. The very first experiments carried out in our group showed that Al NP obtained by conductor electric blast in argon medium and not passed (Fig. 1) reacts with water for several seconds and completely [2].

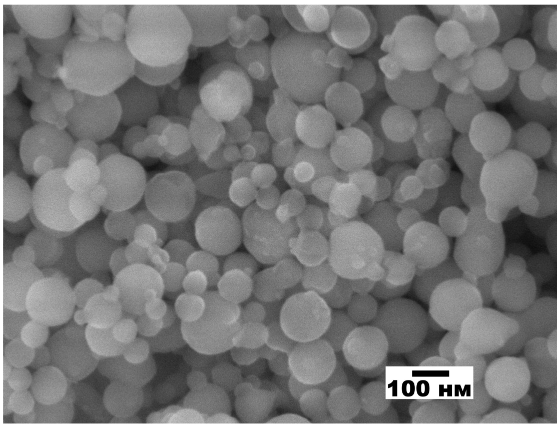

Fig. 1. *Micrograph of aluminum nanopowder*

At water deficiency the interaction results in intensive vaporization and residual NP sintering with products. At the same time, HPE was developed but in low rates, mainly, in the interest of space-based processing and submarine force. Possibilities and manufacturability of obtaining H_2 have been significantly expanded at occurrence of NP with high reactivity. Studying the reaction of Al NP with H_2O the new laws unknown before were determined.

4. Water – global component of hydrogen power engineering

Let us consider in detail some processes of Al NP interaction with H_2O. It is known that compact metal Al – one of the most active metals – is always covered in ordinary conditions with thin continuous oxide film which preserves metal from interactions with oxygen, water vapors, diluted solutions. Crippling oxide film, which may be achieved by processing metals with alkalis and acids, Al starts actively interacting with H_2O. Formally the equation of the reaction of Al with H_2O, nonmetering possible $Al(OH)_3$ transformations, may be given in the form:

$$2Al+6H_2O=2Al(OH)_3+3H_2.$$

This implies that at interaction of two atoms of Al with H_2O three molecules of H_2 are formed, in other words, according to stoichiometric calculations – at interaction of 54 g of Al with H_2O 67,2 l (or 6 g) of H_2 (volume is given for 0 °C and 1 at) and 156 g of $Al(OH)_3$ are formed. The rate of this reaction at room temperature is not high as there is always dissolved oxygen in water which passivates partially metal Al. But at temperature rise as well as in the case of presence of small quantities of alkalis, acids or salts in water the rate of the reaction increases.

4.1. Stored energy in nanoaluminum

Since 1980-s the high rates of interaction, obtained in conditions of electric blast of Al NP with O_2 and H_2O, stimulated a thought about stored energy in NP. Really, individual samples of Cu и Ag NP heated to 300 and 60 °C, respectively, demonstrated heat extraction without change of their own mass [3]. It was not possible to carry out such experiments on Al even in vacuum of 0,01 Pa the sample mass increased. Thermal effects were succeeded to be measured by the methods of combustion in oxygen under pressure of 2 MPa and method of solution in isothermal conditions. Their excess (i.e. stored energy) amounted to 80 kJ per a mole of original NP. In terms of content of metal Al in NP (92...94 wt. %) this value amounts to approximately 100 kJ per a mole of NP. To estimate the peculiarity of this effect it is enough to remember that Al melting heat in massive state equals 13,6 kJ/mole. From the point of view of thermodynamics this result has no explanation: if such energy – 100 kJ is injected into 1 mole of Al it should be melted. The investigations showed that really, such state is possible for NP of studied dimensional range of particle diameter from 60 to 150 nm. Energy is stored in the form of double electrical layer with high pseudo-capacity formed in conditions of electric blast and amplified at passivation.

X-ray structural NP analysis showed that particles have reduced X-ray density on the average by 0,2 %. Such density is achieved at heating massive Al to 70 °C. It is necessary to emphasize that stored energy is not connected with surface energy: for particles with such diameter it does not exceed 4 kJ/mole. At combustion and at chemical reactions the stored energy acts as «starting dope» (release mechanism), reducing process temperature thresholds.

4.2. Is it possible to achieve temperature 400 °C in liquid water?

Thermal condition features of Al NP interaction process with H_2O result in occurrence of new effects which were not known for reaction with Al grits. First of all, it is the self-heating effect of nanoparticles to temperatures exceeding surrounding water temperature by hundreds degrees. Let us consider the reasons of this effect display. Using industrial Al powder ASD-1 the rate of H_2 extraction amounts only to $1,38\cdot10^{-4}$ l/s·g (0,138 ml/s per 1g of powder). In this case only Al 20...30 % of original Al transforms into end product – a mixture of oxides and dioxides [4]. Investigations carried out by our group showed that Al NP exceeds general industrial powders of the type ASD-1 in its reactivity. At the same time, the rate of H_2 extraction at Al NP interaction with distilled water at 60 °C amounts to 3 ml/s·g, at 80 °C – 9,5 ml/s·g, that exceeds the rate of H_2 extraction at hydrothermal synthesis approximately in 70 times. Another advantage of using NP in one reaction is the fact that Al transformation degree amounts to 98...100 % (depending on temperature). Moreover, introduction of even insignificant quantities of alkali into distilled H_2O results in considerable increase of reaction rate: amplifying pH solution to 12 the rate of H_2 extraction rises to 18 ml/s·g at 25 °C. The rate of H_2 extraction at ASD-1 dissolving in solution containing 8 g/l of NaOH, at the same temperature amounts only to 1 ml/s·g. The given data show that Al NP in comparison with compact Al and industrial grits interact with H_2O with high rate and transformation degree ~100 % and their application allows obtaining H_2 at sufficient rate at ordinary conditions.

Reaction of Al with H_2O is exothermal one i.e. heat is released at interaction. The calculations show that at total interaction of 27 g of Al (1 mole) with H_2O with formation of amorphous $Al(OH)_3$ and H_2 by reaction (3) 418 kJ of heat is released. The same quantity of heat is released at combustion of ~13 g of carbon. It is obvious that depending on mass relation of taken Al and H_2O, as well as reaction rate (in other words – heat production rate иными) and rate of heat abstraction into environment, the reaction mixture may have relatively constant temperature and may be gradually heated that results, in its turn, in increase of reaction rate. Let us estimate the temperature to which the mixture of Al NP with H_2O may be heated in the course of reaction. Minimal mass of H_2O, required for total consumption of 27 g of Al forming products according to stoichiometry of reaction (3), amounts to 54 g. The amount of heat, released in this case, without its removal into environment is enough for heating reaction products to the temperature ~2300 °C. Naturally, in practice the reaction is not carried out in such (adiabatic) mode. A small water excess exceeding its stoichiometric quantity, for example, two times, results in sharp temperature decrease due to heating this excess amount of water.

Our group discovered for the first time and experimentally justified the «self-heating effect»: it is temperature excess inside nanoparticles in comparison with environmental temperature in which or with which the chemical reaction occurs [5]. This effect is explained by the presence of significant part of atoms on nanoparticle surface comparable with a part of atoms in particle volume. Heat released in the reaction is accumulated in metal constituent of nanoparticle. Nevertheless, an indirect method of determining maximal temperature of self-heating was found out.

4.3. What else beside hydrogen and heat may be obtained in the reaction of nanoaluminum with water?

The consequence of self-heating of Al NP particles is different chemical and phase state of solid products of its interaction with Al H_2O.

Simultaneously, product composition reflects the value of temperature inside a particle: it is a peculiar temperature test. At present no direct methods for determining temperature inside nanoobjects are developed. The nature turned out to be generous presenting to us a chain of phase transformations of Al oxidation products depending on temperature (Fig. 2). This transformation chain may be taken as a principle of an enterprise manufacturing products of different assortment.

Presence of self-heating of Al nanoparticles and high rate of H_2 formation results in its accumulation on interface of metal-oxide (hydroxide) metal and in rapture of oxide-hydroxide jacket. As a result of these processes the reaction solid products form nanostructures which were not managed to be obtained before using NP. The most surprising fact is the fact that sizes of structural elements – pores, layers – do not exceed 100 nm and in some cases – tens of nm. Micrograph of such product having cellular structure with cell size ~100 nm and barrier thickness between them 10...20 nm is given in Fig. 3. Beside the products with such morphology depending on temperature and hydrodynamic modes of reaction some more types of products differ in structure and chemical composition are managed to be obtained. The most surprising in their morphology are the products consisting of hollow spheres or their fragments with the size not exceeding 100...200 nm. Formation of such «shells» is rather interesting manifestation of so-called chemical-mechanical effect which is also a consequence of Al nanoparticle self-heating at their interaction with H_2O. That is, in comparison with mechano-chemical effect in which chemical reactions occur under the action of mechanical loads, in this case, on the contrary, chemical reaction results in mechanical failure.

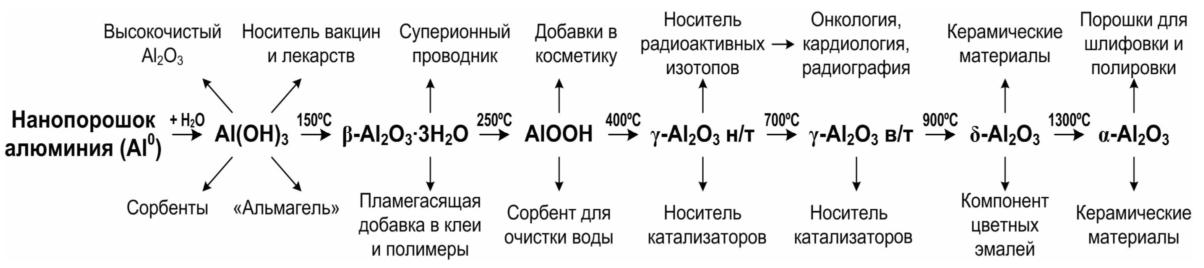

Fig. 2. *Diagram of thermal transformations of interaction products of aluminum nanopowder with water and fields of their application*

Нанопорошок алюминия (Al^0) – Aluminum nanopowder (Al^0); Высокочистый Al_2O_3 – High-clean Al_2O_3; Носитель вакцин и лекарств – Carrier of vaccines and drugs; Суперионный проводник – Superionic conductor; Добавки в косметику – Admixtures into cosmetics; Носитель радиоактивных изотопов – Carrier of radioactive isotopes; Онкология, кардиология, радиография – Oncology, cardiology, radiography; Керамические материалы – Ceramic materials; Порошки для шлифовки и полировки – Powders for grinding and polishing; Сорбенты – Sorbents; «Альмагель» – «Almagel»; Пламегасящая добавка в клеи и полимеры – Flame trapping admixture to clues and polymers; Сорбент для очистки воды – Sorbents for water purification; Носитель катализаторов – Catalyst carrier; Компонент цветных эмалей – Coloured enamel component

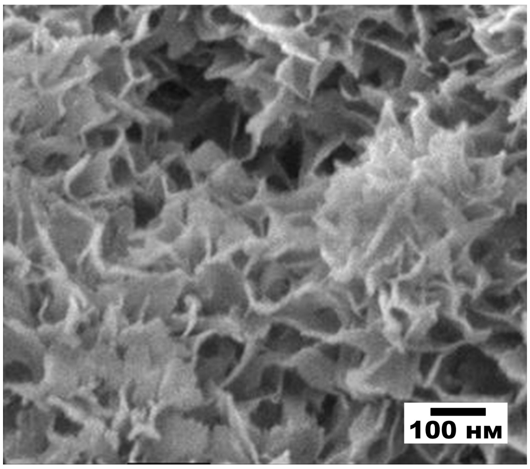

Fig. 3. *Micrograph of interaction product of aluminum nanopowder with water*

The fact of forming hollow spheres consisting of Al (hydr-)oxides of different modifications may be explained in the following way [6]. Thickness of oxide shell on the surface of Al nanoparticles is inhomogeneous and probably, Al interaction with H_2O starts in the places where this shell is thinner. As diffusion problems at interaction are minimal on such part of particle surface, the reaction front is nonuniformly developed and a particle to a large extent is «etched» just from the side of the mentioned area. As a result, when Al is used up, only the «shell» remains from a nanoparticle. It was determined that products with such morphology are obtained in rather mild conditions – at rather high excess of H_2O and reaction mixture temperature not exceeding 70 °C. Mixture temperature rise stimulates, probably, the destruction of such hollow formations and generation of products with cellular structure. Forming fractions of oxide-hydroxide cover has a form of shells (Fig. 4).

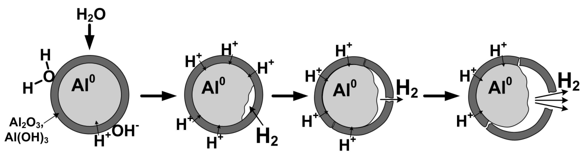

Fig. 4. *Diagram of aluminum nanoparticle interaction with water explaining formation of products with cellular structure*

From the point of view of H_2 generation, the chemical-mechanical effect promotes sharp increase of the reaction rate: rapture of oxide-hydroxide shell results in H_2O penetration directly to metal surface. H_2 is formed on interface of metal-oxide (hydroxide) metal and has high temperature – self-heating temperature and it amounts to hundreds degrees. At 400 °C H_2 is efficiently diffused through a nickel plate with thickness of 10 cm.

4.4. One more effect with nanoaluminum

Can water boil at atmospheric pressure at temperature lower than 100 °C? It turned out that adding Al NP into в H_2O results in decrease of water boiling temperature [7]. The value of this decrease depends on NP activity. If boiling temperature decrease connected with Raoult law then it would depend on Al NP content in water but not on NP activity. Bubbles of H_2 formed as a result of reaction of Al with H_2O are saturated with H_2O vapors, come to the surface where they burst ejecting H_2O vapors into atmosphere. Boiling water temperature was measured by thermocouples and master mercury thermometers. This effect was explained attracting the model of «hot» H_2. H_2 bubble formed on the surface of Al nanoparticle contains inside the H_2 molecules with high kinetic energy which is transferred by H_2O molecules at collision with H_2 molecules initiating, thereby, vaporization on inner surface of gas bubble. The bubble moving to water surface is gradually saturated with H_2O vapors. And when achieved the surface it is damaged ejecting H_2O vapors into atmosphere.

5. From hydrogen power engineering to hydrogen civilization

Why do scientist strive for development of HPE, companies spend annually millions of dollars for studying in this direction, enterprises of machine-building field speak more and more about hydrogen transport production and power engineering specialists consider H_2 the most successful change of hydrocarbon fuel in conditions of more increasing fuel crisis? It seems as if H_2 penetrates into all spheres of our life – it is no coincidence that its molecules have the highest penetrability among other molecules in physical sense as well. H_2 «attractiveness» is explained by its unique properties. Why is not then this unique gas widely used for solving the problems in different manufacturing fields? It happens because its use is associated with a number of difficulties, enumerated above, which are soluble nevertheless. For example, for solving the problem of transporting and storage of H_2, it is sufficient to obtain it at the place of consumption. At present H_2O electrolyzers which are rather bulky and have insufficiently high productivity are used for this purpose that complicates the development of H_2 mobile sources. One of the methods for solving the problems of H_2 transporting and storage may be use of H_2 generators on the basis of Al NP. At interaction of 1 kg of Al NP with H_2O 1244,5 l of H_2 is extracted which gives 13,43 MJ of heat at combustion. The efficiency of such process for obtaining H_2 is higher than in the case of electrolysis – Al NP oxidation occurs by 100% that is the applied material is totally used.

In terms of car consumption of 10 l of oil per 100 km of run it follows that at its total combustion 400 MJ/kg of energy is released. To obtain the same quantity of energy 3,3 kg of H_2 is required; it may be obtained of ~30 kg of Al. Al cost on the world market amounts to approximately 3 USD per 1 kg. Thus, the comparison of the cost for 10 l of oil – 10...15 USD and a cost of 30 kg of Al – 90 USD indicates the necessity of complex solution of HPE problems and implementation of interaction products of Al with H_2O as a commercial product. Growth rate of costs for hydrocarbon raw materials predict optimistically the transfer to HPE.

Power cycle on the basis of Al NP is given in diagram (Fig. 5); it is shown that at Al NP interaction with H_2O

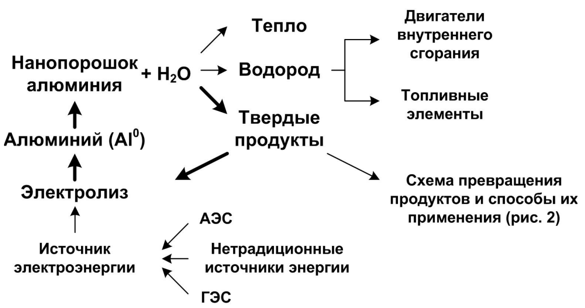

Fig. 5. *Diagram of power cycle: НП Al + $H_2O \rightarrow H_2$ + solid products → electrolysis → Al dispersion → Al NP*

Нанопорошок алюминия – Aluminum nanopowder; Алюминий (Al^0) – Aluminum (Al^0); Электролиз – Electrolysis; Источник электроэнергии – electric energy source; Тепло – Heat; Водород – Hydrogen; Твердые продукты – Solid products; Нетрадиционные источники энергии – Unconventional energy sources; АЭС – AES; ГЭС – GES; Двигатель внутреннего сгорания – Internal combustion engine; Топливные элементы – Fuel elements; Схема превращения продуктов и способы их применения (рис. 2) – Diagram of converting products and methods of their application (Fig. 2)

H_2, heat are released and solid products which may be used as functional materials (Fig. 2) [8] or may be directed to cycling into metal Al with further cycling into NP closing power cycle are formed. This diagram may become the principle one for wasteless technology of gaseous H_2. AES, GES as well as any unnconventional energy source of may serve as external energy source which is required for its functioning.

Conclusion

Complex use of interaction products of Al NP with H_2O, heat utilization and efficient functioning of power cycle on the basis of Al NP is a real technology of gaseous H_2 for HPE of near future. Al NP application gives cogent advantages: the necessity of storing and transporting gaseous H_2 disappears that increases significantly fire- and explosion safety of this fragment of HPE. At industrial manufacturing of Al NP including other directions of its application, its prime cost deceases in several times. At present it is reasonable to apply Al NP in mobile small-size sources of H_2, for example, for hybrid automobile engines, for using in hard-to-reach areas (tundra, deserts, massifs). Al NP may be a basis of HPE for colonies on the Moon as well as a source of H_2 in fuel elements for expeditions directed to Mars. Therefore the problem of technical character – the development of mobile sources of H_2, combined with fuel elements which are necessary for electric energy production is on the agenda.

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