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INVESTIGATION OF THE FEATURES OF HYDROGEN SYNTHESIS BY WATER DECOMPOSITION ON MICRO- AND MACROSTRUCTURED SILICON POWDERS

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This paper presents the results of experimental studies of the process of obtaining hydrogen with the use of micro- and nanostructured silicon powders. From the results of the investigations the optimum size of micro- and nanoparticles of silicon enabling the chemical reaction to proceed without energy expenditure has been established. The efficiency of the chemical synthesis of hydrogen as an alternative source of thermal energy has been shown.

One of the most important problems of modern society is the search for alternative energy sources. The most promising secondary kind of fuel appears to be hydrogen — an ecologically friendly and practically inexhaustible energy carrier. Because of the catastrophic worsening of the ecological state of the planet and depletion of hydrocarbon resources, it is preferable to use hydrogen as an absolutely harmless fuel for transport facilities, for heating homes in remote regions, and in independent and stationary sources of secondary energy.

Wide use of hydrogen will reduce atmospheric pollution, reduce the green-house effect, and, as a consequence, slow down global warming up. In the current hydrogen production, electrolysis of water and its varieties are mainly used [1–7]. According to calculations, from one liter of water 1234.44 dm^3 (liters) of hydrogen can be obtained. However, the changeover of the power industry to hydrogen fuel is inhibited by the large energy expenditures needed for obtaining hydrogen from water. The electrolysis process proceeds at a voltage of 1.6–2.0 V and a current intensity of tens and hundreds of amperes. The most advanced electrolyzers expend more energy for obtaining 1 m^3 of hydrogen than can be obtained by burning it (4 and 3.55 kW·h, respectively). The problem of decreasing the energy expenditures for obtaining hydrogen from water is being addressed in many laboratories in the world, but no significant results have been obtained so far. In the current hydrogen production, several directions which solve in their own way the problem of obtaining it have taken shape [2–4]. For instance, the authors of [5] suggested to decrease the energy consumption in the process of water electrolysis by switching to photoelectrolysis and by conducting the process of water electrolysis in a gravitational field [6].

In obtaining hydrogen by a purely chemical method, most researchers use acids and metals, natural gases, e.g., such as methane, coke gas, as well as gases obtained from oil refining. Of special interest, of course, is water, its decomposition into hydrogen and oxygen. The process of chemical decomposition of water proceeds mainly in the presence of such catalysts as platinum, palladium, hot iron, sodium aluminate tetrahydrate, and sodium amalgam [3].

Of particular interest is the reaction of water with sodium amalgam, in the process of which pure hydrogen and a pure aqueous solution of sodium hydroxide are formed [2]. Consequently, the use of sodium and potassium hydroxide in the presence of silicon will make it possible to decompose water into hydrogen and oxygen. In this case, the oxygen is expended in forming Na_2SiO_3 and K_2SiO_3, respectively, and, taking into account the fact that in the manufacture of semiconductor devices and integrated circuits a large amount of silicon waste has been accumulated

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and is constantly renewed, and their reclamation presents a difficult problem, this is undoubtedly topical. Therefore, the use of semiconductor silicon wastes for hydrogen synthesis appears to be very promising. Moreover, up to now no proper investigations in this field have been carried out.

In the present work, an attempt is made to elucidate the possibility of synthesing hydrogen by a chemical technique as a result of the decomposition of water on micro- and nanostructured silicon powders. To this end, we have performed a series of investigations on estimating the efficiency of the process of water decomposition to hydrogen on micro- and nanostructured silicon powders in the presence of potassium and sodium hydroxides. The results obtained are presented with the example of using potassium hydroxide and sodium hydroxide.

Experimental. Micro- and nanostructured silicon powders with a particle (crystallite) size from 20 to 70 nm were obtained as a result of the decomposition of monosilane (SiH_4) in the chamber volume at a pressure of 20–40 Pa in a modernized plasma plant of the "Plasma 600" type and those with a particle size from 70 to 6000 nm — as a result of the comminution of monocrystalline silicon wastes in a VIM-8 vortex jet-type acoustic mill. The sizes of particles and their quantitative size distribution were determined by means of photographs from an S-806 scanning electron microscope (Hitachi, Japan) and an H-800 transmission electron microscope (Hitachi, Japan). The average sizes of nanoparticles were determined by the diffraction of X-rays by the crystalline nucleus of the particle.

The laboratory setup for investigating the synthesis of hydrogen by decomposing water on micro- and nanostructured silicon powders consists of a molybdenum or quartz glass flask and a system for extracting hydrogen from the flask. It represents a quartz pipe of length 40 mm, wall thickness 2 mm, and outer diameter 5 mm. The pipe was mounted in a special cork, which after charging the flask with the necessary components was connected to the pipe. In the experiments with hydrogen, we used chemically pure sodium and potassium hydroxides and distilled water. The qualitative production of hydrogen was determined by its ignition in the upper part of the pipe by a naked flame (lighter). Quantitative determination of the hydrogen volume was carried out by the method of displacement of the known volume of the liquid from a special vessel and by filling a balloon. The propagation of the flame was recorded by a digital camera connected to a computer. Dosing of components was realized by their weighing on a SETRA EL-200S analytical balance with an accuracy of 10^{-6}.

The reproducibility of experiments was estimated by the Kohren criterion as a result of the statistical data processing with a confidence coefficient of 0.97.

Results: Analysis and Discussion. The process of chemical decomposition of water on micro- and nanostructured silicon powders in the presence of potassium and sodium hydroxides is given by the reactions

$$\mathrm{Si + 2\,KOH + H_2O = K_2SiO_3 + 2H_2}\ \ (\mathrm{gas})\,,$$

$$\mathrm{Si + 2\,NaOH + H_2O = Na_2SiO_3 + 2H_2}\ \ (\mathrm{gas})\,.$$

The material balance of the reaction shows, e.g., that from 28 g of silicon, 112 g of potassium hydroxide, and 18 g of water, 44.8 dm^3 (liters) of hydrogen are formed. From this it follows that if we take 1 dm^3 of water and in the corresponding proportions silicon and potassium or sodium hydroxide, then 2450 dm^3 of hydrogen will be produced. Such a quantity of hydrogen is undoubtedly of interest in the case of using stationary small- or medium-sized setups for its synthesis.

An important characteristic of the process of chemical synthesis is the rate of hydrogen production. The reaction is based on the interaction of three components. The reaction therewith is exothermal and proceeds with thermal energy release to the extent of 196 kJ/mole and does not require preheating of the reaction components. The reaction proceeds at room temperature, and its rate depends on the silicon powder dispersion (Fig. 1). It is seen that in using both micro- and nanostructured silicon powders, as the particle size increases, there is an increase in the hydrogen production rate. Importantly, for nanosized powders an entirely different character of the change in the hydrogen production rate compared to microsized powders is observed. An increase in the size of nanostructured silicon particles from 30 to 70 nm leads to an increase in the hydrogen production rate from 0.1 to 0.3 $dm^3 \cdot sec^{-1}$, whereas going to the microlevel of 100–5000 nm causes an insignificant increase in the hydrogen production rate from 0.30 to 0.4 $dm^3 \cdot sec^{-1}$ and, what is more, a plateau with a particle size of 3000 nm is attained. In the region of nanosizes of silicon powder particles r = 30–70 nm, the hydrogen production rate is related to the particle size by a nonlinear function

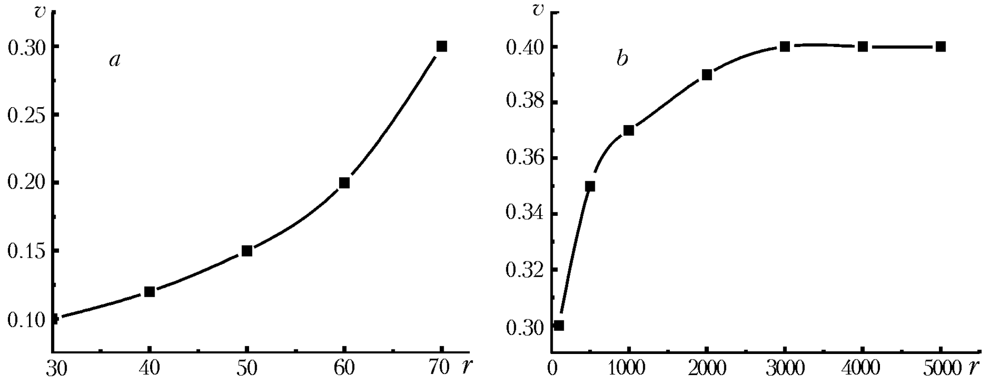

Fig. 1. Hydrogen production rate v versus the dispersivity of silicon powders r: a) nanosize powders; b) microsize powders. v, $\mathrm{dm^3 \cdot sec^{-1}}$; r, nm.

described by a concave curve (Fig. 1a), and in the case of microsize silicon powder particles with $r = 100–5000$ nm, the change in the production rate is described by a mirror-overturned nonlinear function with a slight change in the output parameter.

Apparently, the size of micro- and nanoparticles controls the supply of water and potassium (sodium) hydroxide to the powder volume and, accordingly, the removal of hydrogen from the volume on the whole. It may be suggested that when nanoparticles are used there is a significant increase in the micropowder density, as a result of which a more dense body of fragments-conglomerates is created to inhibit intensive penetration through them of the main components of the reaction into the bulk of the powder layer. In this case, the production rate of hydrogen and its removal decrease. A decrease in the size of micro- and nanoparticles leads to a considerable decrease in the unit volume of the bulk weight of the powder. The final state of the powder is determined by the average size of voids between nanoparticles, through which the reaction components get into the bulk of the powder material. An increase in the size of particles forming a layer of micro- and nanostructured silicon powder leads to the formation of a smaller number of micro- and nanoparticles and a decrease in the area of interfaces with excess energy which promote the penetration of the liquid into the layer volume and an increase in the penetrability for the reaction components. As a result, the absorptivity of powders increases and, consequently, the process of production and removal of hydrogen intensifies. Micrometer sizes of silicon powder particles (≥3000) lead to a stabilization of the hydrogen production process. The influence of micro- and nanoparticle sizes over 3000 nm is immaterial. In this case, it may be concluded that for small nanoparticles (<70 nm) the dominant role is played by the contribution of the surface area, and in the case of microparticles (>100 nm), by the contribution of the volume. The most densely organized nanostructered silicon powders are obtained from the smallest and nanodispersed particles. Thus, to increase the duration of the hydrogen production process in the silicon–water–hydroxide system, it is expedient to use nanodispersed silicon powders (≤70 nm) which make it possible to purposefully control the reaction of hydrogen synthesis by the chemical method, and to retard it, it is necessary to keep the nanoparticles in suspension.

Figure 2 gives photographs showing hydrogen flames at different (flow) rates of the hydrogen produced: the length of the laminar flame increases with increasing hydrogen production rate. As is seen, the intensity of the processes of combustion of hydrogen produced by the chemical reaction of interaction of silicon micro- and nanopowders with water and potassium hydroxide chosen in the proportion 3.0 g of silicon powder, 11.5 g of potassium hydroxide, and 2.0 g of water strongly depends on the hydrogen production rate (particle size). At a hydrogen production rate of 0.15 $\mathrm{dm^3 \cdot sec^{-1}}$ (particle size up to 50 nm) there appears a pike-like flame (Fig. 2a), the duration of its burning is 240 sec and the volume of released hydrogen is 5 $\mathrm{dm^3}$. An increase in the hydrogen production rate to 0.3 $\mathrm{dm^3 \cdot sec^{-1}}$ (nanoparticles of ≤70 nm) leads to an increase in the pike-like flame and a decrease in the duration of its burning to 180 sec. At a hydrogen production rate of 0.3 $\mathrm{dm^3 \cdot sec^{-1}}$ (microparticle size up to 70–100 nm) the flame acquires the shape of a long sharp pike.

The hydrogen combustion process is rather fast: from the moment of ignition to the end of combustion the process proceeds for 120 sec and is accompanied by a loud sound. At the peak of its burning the flame lifts off the pipe and reaches the maximum value of its intensity, and then it begins to drop and dies out. The latter confirms that

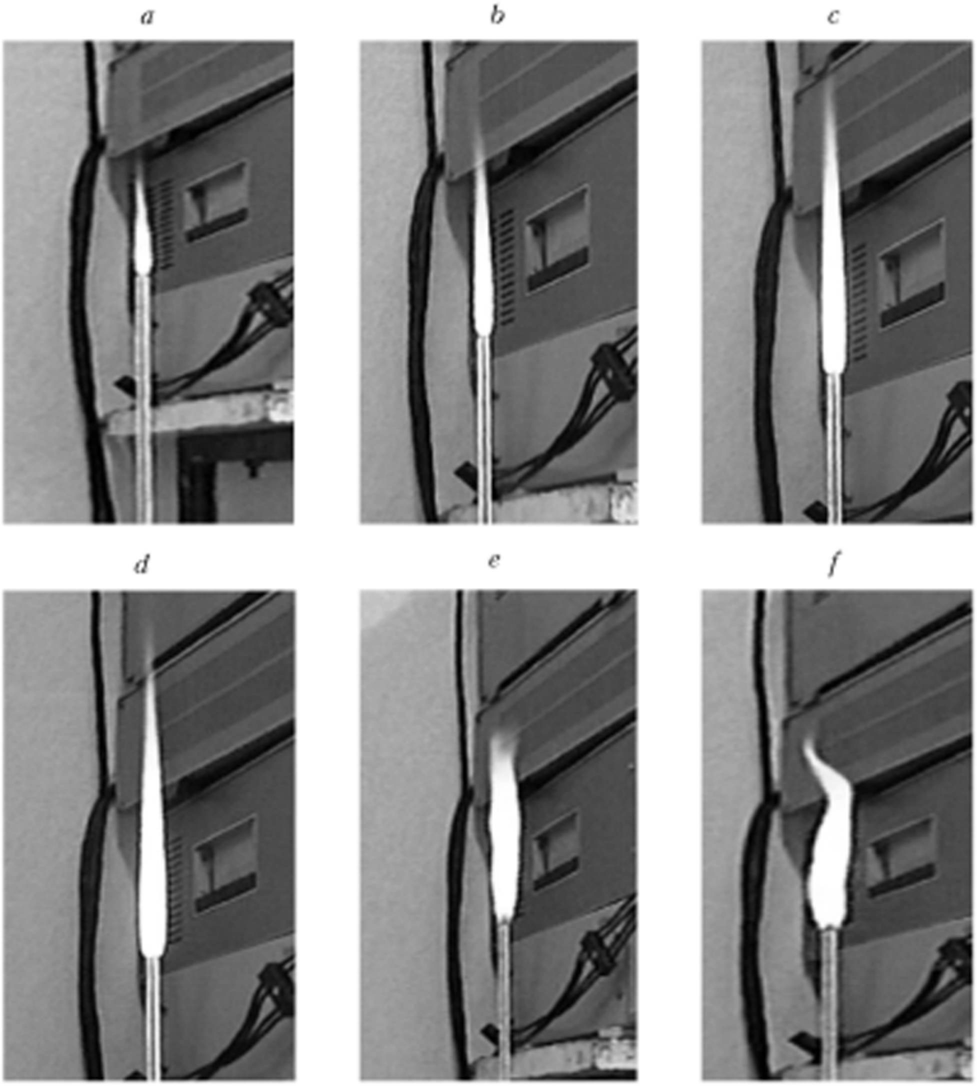

Fig. 2. Length of the laminar combustion flame of hydrogen versus its production rate: a) v = 0.1 $dm^3 \cdot sec^{-1}$; b) 0.2; c) 0.26; d) 0.30; e) 0.35; f) 0.40.

the initial reaction products have been used up and the reaction has terminated. At a hydrogen production rate of 0.37–0.40 $dm^3 \cdot sec^{-1}$ (particle size of 100–5000 nm) the flame of hydrogen combustion changes its shape: it acquires a thickened form of either a cylinder or a bent pike (Fig. 2e, f). The combustion process proceeds for 60–90 sec. The glow is bright as in all the previous cases. This suggests that in all the cases "pure" hydrogen is produced. Premature firing of released hydrogen immediately leads to an explosion with a powerful shock wave and a loud sound. In this case, the flame is drawn into the internal volume of the output pipe and the flame becomes "running." If the pipe is ejected from the front vessel, then the force of the shock wave, as well as the sound intensity, weakens, otherwise the vessel becomes a "bomb." The force of the shock wave and the sound intensity thereby reach their maximum value and there occurs an explosion of enormous force at a volume of produced hydrogen of only 5 dm^3. Intense combustion of hydrogen begins after complete wetting of silicon micro- and nanopowders with water and potassium (sodium) hydroxides and terminates after the initial reaction products have been completely used up. In the precipitate, potassium (sodium) silicate, which can be used as liquid glass, remains.

Thus, the hydrogen combustion processes at different rates of its production (different particle sizes of nano- and micropowders) additionally point to a fairly high efficiency of the process of chemical synthesis of hydrogen as an alternative source of thermal energy.

CONCLUSIONS

1. The rate of hydrogen synthesis on micro- and nanostructured silicon powders is determined by the size of powder particles. In using nanoparticles of size from 30 to 70 nm, a more rapid increase in the rate than at 100–5000 nm has been revealed. At a size of 3000 nm the rate stabilizes and goes to a plateau, i.e., is independent of the micropowder size in the investigated range.

2. To control the hydrogen production rate by the chemical method, it is expedient to use nanosize (≤70 nm) silicon powders and for accelerated production microsize (≥100 nm) silicon powders or nanosize powders but in the suspended state.

3. In the process of hydrogen synthesis, as a result of the chemical interaction of silicon powders, water, and potassium and sodium hydroxides for small (<70 nm) powder particles, the dominant role is played by the contribution of their surface, and in the case of macroparticles (>100 nm) by the contribution of their volume.

4. The chemical decomposition of water on micro- and nanostructured silicon powders in the presence of potassium and sodium hydroxides can be used to synthesize hydrogen.

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