Researching The Process Of Hydrogen Generating From Water With The Use Of The Silicon Basis Alloys

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Keywords: *ferrosilicon, ferrosilicon aluminium, hydrogen, the reaction completeness.*

There was researched the process of hydrogen generating from water with help of the ferrosilicon aluminium and ferrosilicon alloys with additives of the alkaline earth metals.

There was studied the reaction of the considered alloys interaction under changing the NaOH solution concentration from 10% to 13,3% when the initial temperature range was from 90°C to 130°C. There was determined the necessary content of iron and calcium impurities to increase the gas evolution. The recommendations were formulated as to using the alloys of the silicon and iron with barium impurities for hydrogen generating in the gas generators.

Introduction

Currently the hydrogen application areas are widening. It is associated with the qualitative changes in the chemical, machine-building, metallurgical and energy industries. For example, hydrogen is used at the autonomous objects, in particular at the meteorological stations and air balloon organizations, where it is generated from water by an ordinary method using the standard FS-75 ferrosilicon alloy (Fe-20-25, Si-74-80, Al-0.6, Cr-0.5, P -0.05, S-0.03) [1-13]. The silicon is the main element that displaces hydrogen from water in presence of sodium hydroxide.

By this moment, thermodynamics, kinetics and heat-mass transfer have been investigated under interaction of a sodium hydroxide solution with the standard aluminium powders and the aluminium activated with indium, gallium and tin. As to the experiments with the silicon alloys, there were researched the FS-75 ferrosilicon and the ferrosilicon aluminium alloys (FSA).

Purposes and research tasking

The purposes of the research are the following:

- To improve the economically feasible hydrogen generation method using the ferrosilicon alloys with additives of alkaline earth metals and ferrosilicon aluminium;
- To determine the theoretical value of the reaction completeness under interaction of ferrosilicon and ferrosilicon aluminium when the NaOH concentration is changed from 10 % to 13.3 % at the initial temperature range from 90 ºC to 130 ºC;
- To formulate the recommendations on application of the considered method for hydrogen generating in the gas generators.

Experimental results and their discussion

The method of hydrogen generation when using the silicon based alloys is described by the equation [4]

$$Si + 2NaOH + H_2O \leftrightarrow Na_2SiO_3 + 2H_2\uparrow.$$

According to the stoichiometry, it is necessary to take 80g of the sodium hydroxide for every 28g of the silicon. But the practice of hydrogen generation, especially in the high pressure gas generators, has shown that the amount of sodium hydroxide can be much less, since the hydrolysis of the sodium silicates is according to the equation

$$2Na_2O{\cdot}SiO_2 + H_2O \leftrightarrow 2NaOH + Na_2O{\cdot}2SiO_2.$$

As a result, the free sodium hydroxide is liberated and sodium silicate is formed with a module of n = 2. In the technical area of knowledge the sodium silicates are usually called as the soluble glass, and their solutions – as the liquid glass. The main characteristic of the soluble glass is the number *n*, which shows how many the silicon molecules SiO_2 is charged per one molecule of the sodium oxide Na_2O. The sodium silicate with n = 2 can be further hydrolyzed with forming the silicates with a larger module. The solution of silicates in water can be in general represented by the formula $Na_2O{\cdot}nSiO_2{\cdot}mH_2O$, where *m* is the number of those water molecules that are included in to the silicates [14].

The main kinetic studies are carried out in the reactor, which provides isochronous driving the process ($V = 1.13{\cdot}10^{-3}$ m^3). As the main hydrogen generating alloys, there were selected (the mass fraction,%): FS 90 -Fe-4.0, Si-92, Al-3.0, Ca-1.0; FS 90 Ba4 - Fe - 5.9, Si - 88.6, Ba - 4.0, Ca - 1.5; FS 75 Ba1 - Fe - 19.3, Si - 78.4, Al - 1.3, Ba - 1.0; FSA 4 - Fe - 5.8, Si - 90.4, Al - 3.8; FSA 30 - Fe - 10.3, Si - 59.9, Al - 29.8; FSA 32 - Fe - 5.5, Si - 62.3, Al - 32.2.

The results of the main series of the experiments are presented in Tables 1-2 and in Figures 1-3.

The reaction is monitored by increasing the pressure in the reactor. The released gas amount is fixed by the gas meter of GSB-400 type. The degree of conversion α_T is defined as the ratio of the released hydrogen maximum volume and theoretically possible one.

$$\alpha_T = V_r/V_T,$$

where V_r is the led to the normal conditions amount of hydrogen released during the reaction; V_T is the volume of hydrogen released under the interaction of m kg of a pure element (Si or Al) with water. For the alumina compounds V_T is determined by the rule of additivity for the alloy active part.

Table 1. Dependence of the hydrogen evolution speed and the FSA - FS alloys reaction completeness on the sodium hydroxide concentration and the initial temperature t = 90 °C. The alloys disperse composition is (0.5-1.5)·10^{-3} m, $m = 5\cdot10^{-3}$ кg.

№	Alloy type	Caustic soda concentration, mass fraction, %	Maximum temperature, t_{max}, °C	Reaction time $\tau\cdot10^{-3}$, sec.	Maximum reaction speed $W\cdot10^3$, м³/(кg·sec.)	Reaction completeness α, %
1 2	FS 90	10 13,3	102 104	5,7 5,4	0,017 0,02	46 48
3 4	FS 90 Ba4	10 13,3	102 105	2,94 3	0,18 0,12	48 50
5 6	FS 75 Ba1	10 13,3	105 104	2,4 1,5	0,009 0,16	45 60
7	FSA 4	13,3	107	3,3	0,8	60
8 9	FSA 30	10 13,3	91 94	4,92 4,8	0,42 0,46	28 30
10	FSA 32	13,3	104	3,6	0,17	54

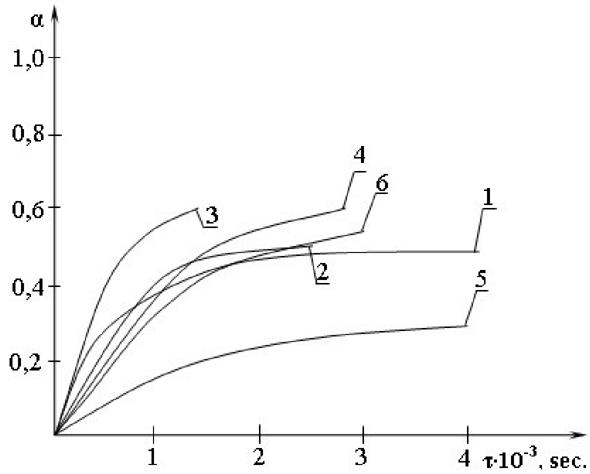

Figure 1. Dependence of the reaction completeness on the time τ under 13.3 % sodium hydroxide concentration and the initial temperature t = 90 °C for the alloys 1-FS 90; 2 - FS 90 Ba4; 3- FS 75 Ba1; 4 - FSA 4; 5- FSA 30; 6 - FSA 32.

Table 2. Dependence of the hydrogen evolution speed as well as the FSA and FS alloys reaction completeness on the sodium hydroxide concentration under initial temperature 130°C. The alloys disperse compositionis (0.5-1.5)·10^{-3} m, $m = 5\cdot10^{-3}$ кg.

№	Alloy type	Sodium hydroxide concentration mass fraction, %	Max. temperature t_{max}, °C	Reaction time $\tau\cdot10^{-3}$, sec.	Reaction speed $W\cdot10^3$, m³/(кg·sec.)	Specific Gibb's energy $-G$, кJ/кg	Reaction completeness α, %
1 2	FS 90	10 13,3	136 133	1,68 2,04	0,75 2,4	17453,7	67 89
3 4	FS 90 Ba 4	10 13,3	139 138	0,9 2,1	0,95 1,07	16141,2	74 82
5 6	FS 75 Ba 1	10 13,3	135 142	1,26 1,23	0,096 0,95	10115,9	52 70
9 10	FSA 4	10 13,3	134 137	2,6 2,4	0,61 1,5	13070,4	80 99
11 12	FSA 30	10 13,3	133 135	3,66 1,68	2,1 3,9	13156,3	51 63
13 14	FSA 32	10 13,3	131 133	3,6 3,48	0,07 0,53	14274,3	49 60

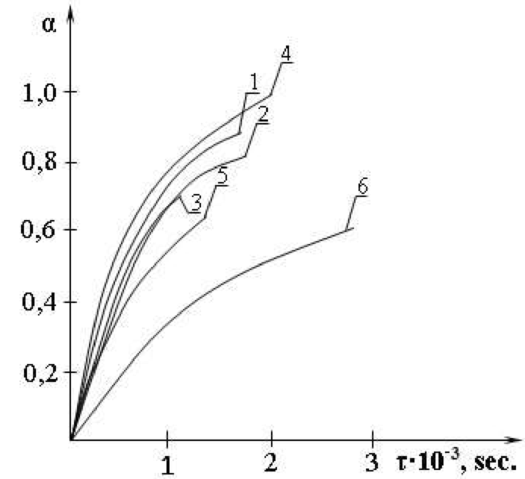

Figure 2. Dependence of the reaction completeness on the time τunder 13.3 % sodium hydroxide concentration and the initial temperature t = 130 °C for the alloys: 1 - FS 90; 2 - FS 90 Ba4; 3 - FS 75 Ba1; 4 - FSA 4; 5 - FSA 30; 6 - FSA 32.

Dependence of the reaction completeness on the time τ under 13.3 % sodium hydroxide concentration and the initial temperature t = 130 °C for the alloys The diagram of pressure increase in the reactor when the alloys are interacted with a NaOH aqueous solution is shown in Figure 3.

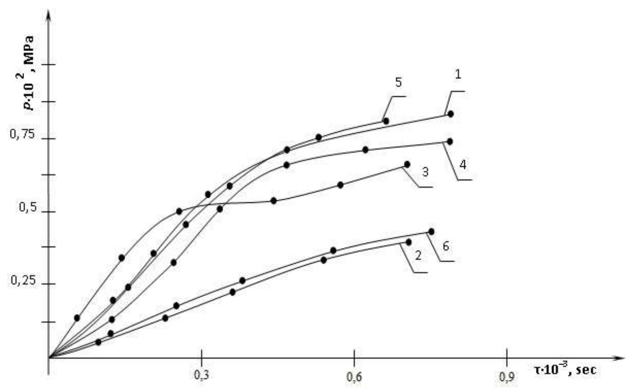

Figure 3.The diagram of pressure change in the reactor (V = 1.13·10^{-3} m^3) when the alloys are interacted with a NaOH aqueous solution of 13.3%, m = 1·10^{-3} kg: 1 - FS 90; 2 - FS 90 Ba4; 3 - FS 75 Ba1; 4 - FSA 4; 5 - FSA 30; 6 - FSA 32.

The high reaction speeds correspond to the high absolute values of the Gibb's *(ΔG°)* energy at the same temperature - table 2.

For the reactions taking place under isobar-isothermal conditions, the possibility of chemical and phase transformations in a closed system is determined by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S,$$

where ΔH is the enthalpy change, J/kg; ΔS – the entropy change, entropy, J/(kg·K); T - temperature, K.

The rate of hydrogen evolution is calculated according to the formula

$$W = \frac{\Delta V}{m \cdot \Delta \tau},$$

V - the volume of generated hydrogen, m^3; Δτ - the time for evolution of this gas volume, seconds; m - is the alloy mass, kg.

The negative values of the Gibb's energy change indicate a high probability of the gas evolution reactions when the FS and FSA alloys are interacted with a NaOH aqueous solution. The FS 90 and FS 90 Ba4 alloys are characterized with the higher gas evolution speed and reaction completeness, than FSA 30 and FSA 32 alloys, which are made by smelting the pure components (Fig. 2-3, Table 2). The alloy FS 90 has got the maximum evolution speed of W_{max} = 2.4·10^{-3} m^3/кg·sec. and the reaction completeness of α = 0.89 in the alloys dispersed composition (0,5 - 1,5)·10^{-3} m and 13.3 % NaOH. The FS 90 high activities due to presence of the calcium and aluminum in its composition that results in increasing the hydrogen evolution speed and reaction completeness (Fig. 2-3, Table 2). At 10 % concentration of the caustic soda, the FS 90 gas evolution speed is W_{max}= 0.75·10^{-3} m^3/кg·sec. and α = 0.67, as well as the FSA 30 alloy gas evolution speed is W_{max}= 2.1·10^{-3} м^3/кg·sec. and α_T = 0.51 - table 2. The speed decrease is obviously due to the blurring of the aluminum hydroxide formed on the alloys surfaces.

Under increasing the initial temperature from 90 to 130 ºC, the gas evolution speed increases significantly for the alloys with a silicon content of more than 75% (FS 90, FS 90 Ba4, FS 75 Ba1, FSA 4) (Fig. 1-2, Tables 1-2).

The results of the experiments with the FS 90 and FS 90 Ba4 alloys containing the iron and calcium show that the rate of their interaction with a sodium hydroxide aqueous solution is higher than the FSA alloys interaction rate - (Fig. 1-2, Tables 1-2). With temperature increasing the calcium, which is the alloys part, rapidly displaces hydrogen from water forming the $Ca(OH)_2$ dihydroxide. The gas evolution is increased only under relatively small additions, namely, iron is of 3 - 5 % and calcium is of 1 - 10 %. We have established this regularity and it corresponds to the data of the paper [15].

When the sodium hydroxide concentration is decreased from 13.3 to 10 % at the same temperature, the FS 90 Ba4 alloy reaction completeness is higher than the FS 90 reaction completeness - table 1. This indicates that the contacting with water barium forms its alkaline environment, which provides the possibility for reducing the sodium hydroxide consumption by 10-15 % and for increasing the amount of generated hydrogen.

The temperature increase from 90 to 130ºC leads to the 1.5-2 times reaction completeness increase for the most alloys. At the same time, the reaction speed increases significantly. The main factor that affects the reaction under interaction of the ferrosilicon alloys with the barium additions is the presence of the silicon barium compounds ($BaSi_2$) in their structure, which interact with water by the following reactions

$$BaSi_2 + 6H_2O \leftrightarrow Ba(OH)_2 + 2SiO_2 + 5H_2\uparrow;$$

$$BaSi_2 + 5H_2O \leftrightarrow BaO{\cdot}2SiO_2 + 5H_2\uparrow.$$

With increasing the reaction temperature of more than 130 ºC, the silicon barium compounds are destroyed, while the reaction products are freely removed from the gas generator. Therefore, under hydrogen generation in the reactors operating at atmospheric pressure and temperatures up to 100 ºC, the presence of alkaline earth metals in the alloys is undesirable. Therefore, under hydrogen generation from water when using the silicon-based alloys with impurities of alkaline earth metals, the reaction products unload process is simplified that greatly improves the process of the autonomous hydrogen generators maintenance.

Conclusions:

[1] Under increasing the initial temperature from 90 to 130 ºC, the gas liberating speed increases significantly for alloys with a silicon content of more than 75% (FS 90, FS 90 Ba4, FS 75 Ba1, FSA 4). The speed decreasing is obviously due to the blurring of aluminum hydroxide formed on the alloys surfaces.

[2] The crystalline FS alloys containing barium and calcium in their composition are the more active than FSA 30 and FSA 32 alloys. Reducing the sodium hydroxide concentration from 13.3 to 10 % for the FS 90 Ba 4 and FS 75 Ba1 alloys gives the possibility for increasing their reaction completeness up to 12-15 % compared to the FS and FSA alloys reaction completeness.

[3] The temperature increase from 90 to 130 ºC leads to the 1.5-2 times reaction completeness increase for the most alloys. At the same time, the reaction speed increases significantly. Under hydrogen generation in the reactors operating at atmospheric pressure and temperatures up to 100 ºC, the presence of alkaline earth metals in the alloys is undesirable.

[4] Application of the alloys with barium additives in a hydrogen generator gives the possibility for approximately 10-15 % reducing the caustic soda consumption and for reducing the harmful substances emissions into environment. At the same time, the reaction products are freely removed from the gas generator.

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