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ALLUMINIUM NANO-POWDER OXIDATION IN LIQUID WATER AT HEATING

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It is shown as aluminium nanopowder content in aqueous suspension influences its oxidation condition by liquid water. Aluminium oxidation process is stated to be characterized by following breakdown time and under certain conditions by aqueous suspension self-heating as well as heat and hydrogen eliminating after aqueous suspension heating to 64...66 °C. To obtain maximal oxidability level of aluminium nanopowder in the conditions of the given experiment it is necessary to adhere to the ratio (in mass parts) H_2O:Al=8:1...25:1.

Introduction

Natural resources depletion of energy carries requires a change-over to ecological and renewable energy. Prospects of applying hydrogen as a source of energy stipulate search and development of qualitatively new methods and technologies. Engineers continue searching for more effective and medium-priced means of molecular hydrogen production [1], and in this respect, aluminium water interaction is perspective [2, 3]. Aluminium is comparatively nontoxic and medium-priced, it being widespread in nature and produced in industry in large quantities by means of electrolysis.

Industrial aluminium powders, as well as solid aluminium, are covered with protective oxide-hydroxide film, for example, ASD-1 powder (particle diameter is ~100 mkm) contains 0,5 wt. % of oxide, it conforms to average thickness of more than 14 mkm film. This film considerably fixes the combustion, namely at the oxidizer diffusion loss of rate towards metal aluminium surface.

Aluminium in the form of nanopowder has low reactivity at room temperature [4] due to its thick oxide-hydroxide cover representing double electric layer [5]. Thickness of oxide film for aluminium nanoparticles with the diameter ~100 nanometers is 2...8 nm. In this case its growth is limited by electric potential which prevents from protons diffusion through the oxide layer to metal. Aluminium nanopowders properties have been studied not well enough that hinders their application as energy carriers.

According to stoichiometric calculation by equation of chemical reaction it is necessary 54 g (3 mole) H_2O for completing oxidation of 27g (1 mole) of aluminium [6], that is water mass is to be twice as much as mass of aluminium: H_2O:Al=54:27=2:1 (equation):

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2\uparrow$$

Al metal reaction with water is exothermic, in this case specific thermal effect is 459,1 kJ/mole of aluminium. Due to heat release at the boundary Al/H_2O, first of all, nanoparticles themselves are heated and then water is heated as reactionary environment [7]. Water temperature rise to its boiling point (100 °C) requires additional quantity of water for Al oxidation because of water evaporation.

The aim of the given paper is to define agents optimum mass ratio: H_2O and Al nanopowder to perform the reaction. In this case the basic test of aim achievement estimation is residual aluminium content in reaction products, which, in its turn, should be more than 1...2 wt. %, and also maximum speed of hydrogen release, but if it does not result in nanopowder sintering in water.

Experimental technique

Aluminium nanopowder has been studied in the research. It is obtained in Tomsk High Voltage Research Institute (Russia) by means of wire electrical explosion (WEE) in the medium of gaseous argon with the addition of hydrogen (10 vol. %) at excess pressure $1{,}52\cdot10^5$ Pa, at capacitive accumulator charging voltage 24 kV (aluminium wire diameter 0,3 mm, length – 75 mm). After nanopowder production passivation by air at slow oxidation of nanopowder is performed to make it more stable in air.

On basis of electroexplosive aluminium nanopowder and warm distilled water (50 °C) aqueous suspension samples at mass ratio H_2O:Al=(6...100):1 have been prepared. Having been stirred continuously in a heat-resistant glass suspension is warmed up to 64...66 °C (magnetic stirrer with heating), after that suspension warming up continues without heating (magnetic stirrer without heating). As a temperature sensor where temperature is registered with electronic chart-recording potentiometer «KSP-4», chromel-alumel thermocouple (wire diameter 0,3 mm) is used. Temperature measurement is carried out from the beginning of suspension heating (~50 °C) till its cooling down.

After reaction water excess is removed by the method of decantation and products are dried at air temperature 25 °C. Diffractometer Rigaku D-MAX/B is applied for determining phase composition of hydrothermal interaction products. X-ray diffraction patterns are recorded using CuK_α-emission in the range of angles 2θ from 20 to 100°.

Aluminium content in initial powders and reaction products is determined by volumetric method – according to hydrogen volume released after samples and deca-molar alkali solution interaction.

Experiments results and their discussion

It is known that aluminium nanopowders oxidation process by water can be intensified by means of suspension heating [8]. In the given technique the temperature 64...66 °C (fig. 1) to which suspension «Al+H_2O» is heated has been chosen: at this temperature proceeding of aluminium oxidation reaction is possible with subsequent spontaneous particles heating and water temperature rising. When heating suspension at lower temperature, the oxidation process is proceeding slower and without suspension self-heating. Suspension heating to the temperature higher than 66 °C resulted in abrupt acceleration of self-heating process without breakdown time which is difficult for recording temperature dependence and determining aluminium oxidation process parameters.

As a result of this experiments it is stated that at continuous stirring of aluminium nanopowder suspension heated to 64...66 °C (fig. 1, area *a*) and absence of external heating source (fig. 1, area *b*) thermal process is characterized by specified breakdown time (τ) and comparatively sharp temperature rising with its maximal value obtaining (fig. 1, T_{max}). After maximal temperature obtaining suspension color is changed from black (aluminium nanopowder color) to light grey (suspension color after oxidation).

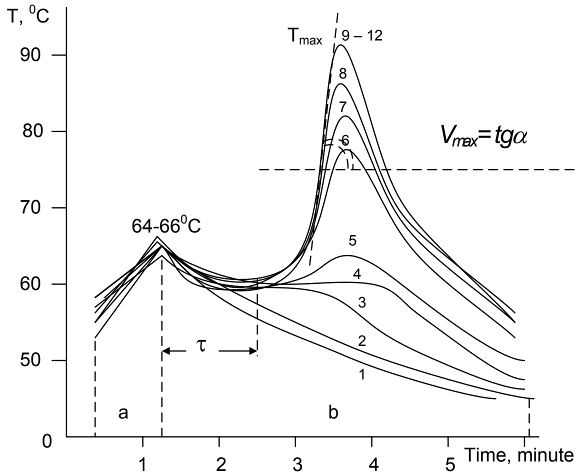

Fig. 1. *Temperature change in time at aluminium nanopowder and water interaction: a) simultaneous heating and stirring of suspension; b) only stirring of suspension; τ – breakdown time, min; V_{max} – maximal rate of temperature rising, °C/s; T_{max} – maximal value of suspension (water) temperature; 1,2,...,12 – suspensions numbers with various aluminium content (table)*

Maximal temperature of suspension at aluminium water interaction depends sufficiently on aluminium nanopowder content in it. At ratio H_2O:Al=(84...126):1 aluminium oxidation process proceeds slowly and without suspension heating (table, samples №№ 1–3), in this case after nanopowder oxidation a lot of unreacted water remains. Increasing nanopowder content in suspension to the ratio H_2O:Al=(56...72):1 self-heating is not registrated (fig. 1, table, samples №№ 4, 5) but aluminium oxidation is indicated by both hydrogen emission and presence of aluminium hydrates in dried product according to the data of X-ray phase analysis. At the same time there is a large quantity of metal Al in these samples i.e. aluminium nanopowder in suspension with the ratio H_2O:Al=(56...72):1 is acidified partially. For suspensions with the ratio H_2O:Al=(8...25):1 self-heating with intensive heat generation (fig. 1, table, samples №№ 9–12) and formation of solid products of aluminium oxidation – aluminium hydrate and boehmite with a very small content of aluminium (fig. 2) are typical. Further increase of aluminium nanopowder content in suspension on attainment of ratio H_2O:Al≤(6...7):1 resulted in temperature 100 °C being reached at aluminium oxidation as a result of self-heating in suspension. In this case there is intensive water evaporation – required oxidizing agent of Al nanopowder in the conditions of the experiment (table, sample № 12).

Table. *Water and Al nanopowder interaction process parameters*

Suspension sample, №	Ratio H_2O:Al by mass* (±0,5 %)	Maximal rate of temperature rising V_{max}, °C/sec	Suspension maximal temperature, T_{max}, °C	Al° content in products, wt. %** (±0,5)	Observations
1	126:1	–	–	–	H_2 emission is not noticeable
2	101:1	–	–	–	
3	84:1	–	–	–	
4	72:1	0,00	60	3,13	H_2 bubbling
5	56:1	0,18	62	2,28	
6	50:1	0,42	78	1,80	Water foaming and hydrogen release
7	42:1	0,53	83	1,66	
8	33:1	0,68	87	1,44	
9	25:1	0,83	92	1,43	
10	16:1	0,83	92	1,43	
11	13:1	0,84	92	1,42	
12	8:1	0,85	92	1,42	
13	7...6:1	1,27	110...115	70,3	Water evaporation

**here and then notation H_2O:Al means proportion of mass of water and aluminium nanopowder;*
***Al° content in initial aluminium nanopowder – 78,2±0,3 wt. %*

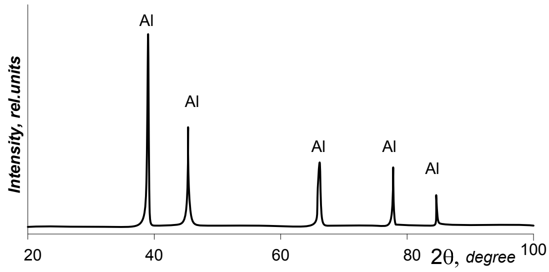

Fig. 2. *X-ray of electroexplosive aluminium nanopowder*

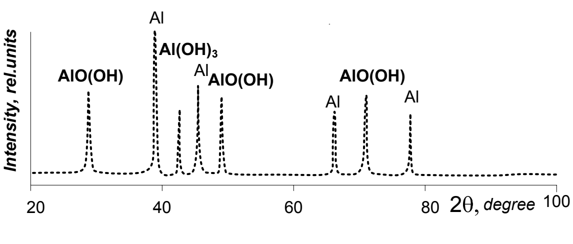

Fig. 3. *X-ray of aluminium nanopowder and water interaction product in suspension of sample № 12 (table)*

Comparing the results being obtained experimentally with the results of calculation according to equation of chemical reaction it should be noted that stoichiometric calculation does not allow the determination of real ratio «H_2O:Al» in suspension sufficient for complete oxidation of Al. Moreover, in the case of applying powdery aluminium at lack of water in similar conditions process of powder sintering is possible [9].

As it was mentioned before electroexplosive metals nanopowders are distinguished for high reactivity when heating. So even at ratio H_2O:Al=6:1 suspension self-heating and oxidation processes are accompanied by intensive water evaporation and nanopowders sintering.

Conclusion

1. Oxidation process of the studied aluminium nanopowder by liquid water in suspension heated to 64...66 °C is characterized by breakdown time and self-heating with heat and molecular hydrogen emission.
2. It is shown experimentally that calculated ratio H_2O:Al=2:1 is not sufficient for reaction of aluminium nanopowder oxidation by liquid water.
3. It is determined that for complete oxidation of aluminium nanopowder (Al residual content is 1,42...1,43 wt. %) for suspension preparation it is necessary to hold the correlation: H_2O:Al=(8...25):1 (wt. %).

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