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The Effect of the Self-Heating Rate on Hydrogen Generation in Quasi-Adiabatic Systems “Aluminum Nanopowder – Water”

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1 Introduction

Studies of the interaction of aluminum nanopowder (ANP, a_s = 100 nm) with water are conducted to determine the physicochemical properties of ANPs themselves, prepare ecologically friendly reactive monofuels (whose condensed combustion products are aluminum oxides and hydroxides) [1,2] and high-porosity oxide hydroxide structures (metalloceramic and filtering materials etc.), and design mobile hydrogen sources on the basis of ANP hydroreaction systems for combustion or catalytic oxidation. Chemical reagents that decompose with the release of hydrogen are of the greatest interest as mobile hydrogen generators. The largest amount of hydrogen is contained in alkali metal hydrides and borohydrides (LiH, NaH, LiBH, and NaBH). Hydrides are, however, hydrophilic, and borohydrides are toxic. Alkali metals are reactive, expensive, and require storage under organic liquids. They vigorously react with water in the combustion mode (with the ignition of hydrogen released). Conversely, group IV–VII metals are unreactive toward water. The Al and Mg metals are of interest for creating mobile “hydrolysis” sources of hydrogen. Their properties are stable, and hydrolysis products are not toxic. The problem with using compact Al and Mg in reactions with water is their low activity (passivation of metal surfaces with insoluble compounds during hydrolysis). It was found in preliminary experiments that the hydrolysis of aluminum plates or magnesium and aluminum–magnesium alloy powders can be performed in solutions in alkalis at pH 11–12. Ideally, a hydrogen-generating system should consist of only two substances, a reducing agent (metal) and oxidizer (water), and hydrogen release should begin at room temperature. The “water–Al” system is capable of producing 1.2 liters of H_2 per 1 g of aluminum under normal conditions. Studies directed to the optimization of the characteristics of systems “water–Al” concentrate on the problem of increasing the reactivity of aluminum powder. For instance, coarse-grained aluminum powders (aluminum spherical disperse ASD-1 and ASD-4, aluminum powder, and aluminum pigment powder) passivated with paraffin completely react with 5 % aqueous NaOH during several months and are of no interest for designing mobile hydrogen sources. ANPs passivated, for instance, with Al_2O_3 are fully hydrolyzed in 5 % aqueous NaOH in 1–2 min [3]. If a solution does not contain alkali, solution temperature increasing from 20 to 80°C results in an explosive reaction between ANP and water [4]. The hydrolysis of ANP yields insoluble

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aluminum oxides and hydroxides, but their high dispersity does not interfere with the supply of new liquid oxidizer portions to the fresh surface of aluminum. In this work, we studied the influence of heating temperature, medium pH, admixtures of metal cations, and the type of passivating coating on ANP on the kinetics of self-heating in reactions between aluminum nanopowders and water. The objects of study (ANP) were nanopowders prepared by the electrical explosion of wires [5]; these powders are produced on an industrial scale, their properties are stable, and the content of metal in them does not change during 5–6 years [6].

2 Experimental Part and Discussion

Aluminum nanopowders

The ANPs were prepared by electrical explosion in gaseous argon with 10 vol. % hydrogen at an excess pressure of 0.15 MPa. The diameter and length of aluminum wires were 0.3 and 75 mm, respectively. After the preparation of ANP, it was passivated by slow oxidation with air (particles were coated with aluminum oxide) and various reagents, including nickel, boron, fluorine, and aluminum stearate and oleate (Table 1).

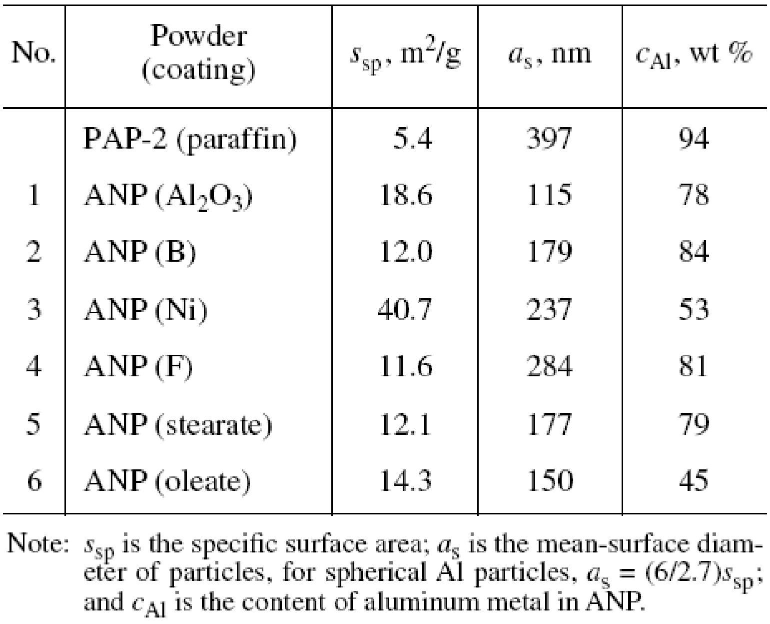
H_2O–ANP suspensions

Aqueous suspensions were prepared from ANP and warm (~50°C) distilled water, and various reagents and additives were introduced into them. A suspension was continuously stirred and heated in a thermostat to 64–66°C , and stirring was then continued without heating. Temperatures were measured from the beginning of suspension heating (~50°C) to its cooling after reaction termination (~25°C). The reaction products were dried in air at room temperature and analyzed.

An analysis of the phase and chemical composition and morphology of the reagents and products

The phase composition of reaction products was determined on a Rigaku D-MAX/B diffractometer. The content of aluminum metal in ANP and reaction products was determined volumetrically, from the volume of hydrogen released in the reaction of samples with a 10% solution of NaOH. The microstructure of initial ANPs and hydrolysis products was studied using a JEOL 6500F scanning electron microscope. The specific surface area of initial powders and hydrolysis products was measured by the Brunauer–Emmett–Teller (BET) method on an ASAP 2020 instrument.

Table 1: **Characteristics of ANP and, for comparison, industrial PAP-2 powder (scaly particles, GOST (state standard) 5494-95)**



No.	Powder (coating)	s_{sp}, m^2/g	a_s, nm	c_{Al}, wt %
	PAP-2 (paraffin)	5.4	397	94
1	ANP (Al_2O_3)	18.6	115	78
2	ANP (B)	12.0	179	84
3	ANP (Ni)	40.7	237	53
4	ANP (F)	11.6	284	81
5	ANP (stearate)	12.1	177	79
6	ANP (oleate)	14.3	150	45

Note: s_{sp} is the specific surface area; a_s is the mean-surface diameter of particles, for spherical Al particles, $a_s = (6/2.7)s_{sp}$; and c_{Al} is the content of aluminum metal in ANP.

The characteristics of passivated ANPs

A decrease in the specific surface area of samples 4, 5, and 6 (Table 1) passivated in fluorinated dodecanol and stearic and oleic acids, respectively, compared with samples 1–3 passivated by the “dry” method is related to a substantial amount of residual solvents on particles (Table 1). This is substantiated by a decrease in the content of aluminum in samples 4–6 and 3. The decrease is maximum for aluminum nanopowder passivated by stearic acid (up to 45 wt %). Coating with organic reagents substantially decreases specific metal contents in powders. With a boron coating, the decrease is less substantial. For ANP coated with nickel, metal content is low, but the specific surface area is high.

ANPs in the reaction with water

According to the stoichiometry, the complete oxidation of 27 g (1 mol) of Al requires 54 g (3 mol) of H_2O (1).

$$Al + 3H_2O \rightarrow Al(OH)_3 + (3/2)H_2\uparrow + 459\ kJ. \qquad (1)$$

Because of heat release in the reaction, the temperature of the mixture increases. When an “open” reaction system is heated to 100°C, the oxidation of Al requires an additional amount of water because of its intense vaporization.

The influence of heating on the kinetics of heat release in the H_2O–ANP system

In spite of the high chemical activity of ANP, the oxidation of aluminum with water must be initiated, because aluminum nanoparticles are always coated with a passivating oxide film. The oxidation of ANP with water was intensified by heating suspensions. The temperature of heating (64–66°C) was adjusted experimentally (Figure 1). At this temperature, spontaneous suspension self-heating began because of heat release in the chemical reaction. When suspensions were heated to lower temperatures, the rate of oxidation was comparatively low, and the reaction occurred without self-heating. Heating above 66°C caused a rapid acceleration of self-heating without an induction period, which complicated recording thermograms of the hydrolysis of ANP. When an H_2O–ANP suspension heated to 64–66°C was continuously stirred (Figure 1, I) in the absence of external sources of heating (Figure 1, II), the thermal process was characterized by induction period τ followed by an increase in temperature to its maximum value *T* max (Figure 1). After this, the colour of the suspension changed from black (the colour of ANP) into light gray (the colour of suspensions after oxidation).

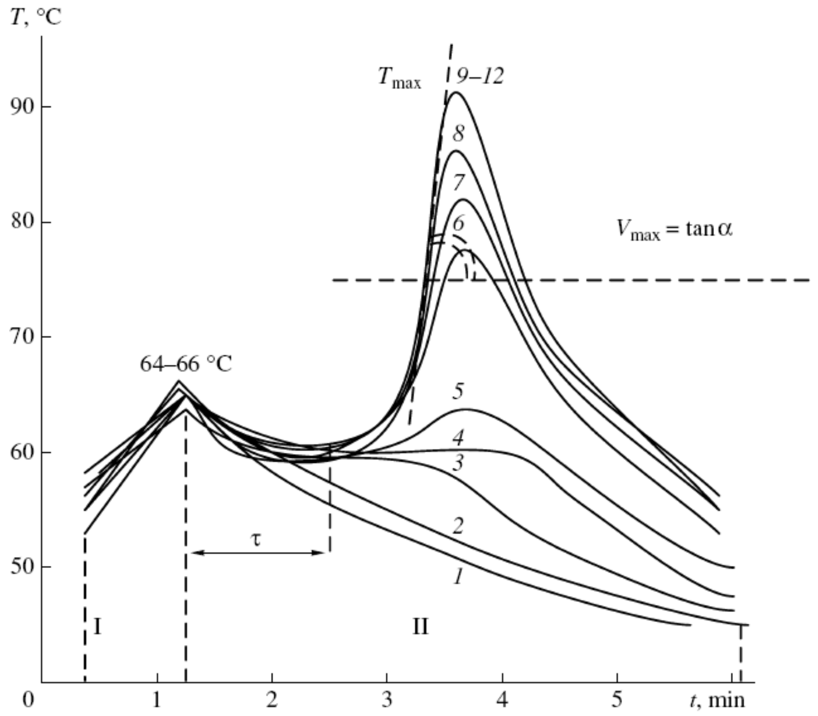
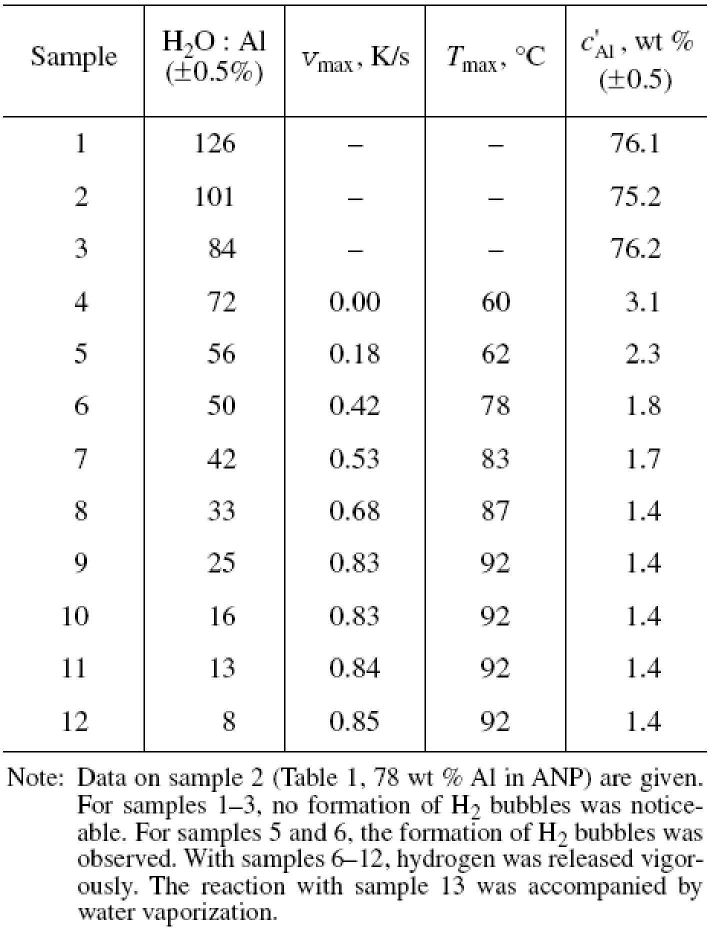


Figure 1: Kinetic curves of temperature variations during the interaction of ANP with liquid water; I, simultaneous suspension heating and stirring; II, suspension stirring only; τ is the induction period, min; v_{max} is the highest temperature growth rate, K/s; T_{max} is the highest suspension (water) temperature; 1,2, …, 12 are suspension numbers with different ANP contents (Table 2)

The maximum suspension self-heating temperature when ANP interacted with water depended on the content of ANP. At an H_2O : ANP ratio of from 84 to 126, the process occurred at a low rate and without suspension self-heating (Table 2, samples 1–3). At higher ANP contents (H_2O : ANP = 56–72), no self-heating was recorded (Figure 1, Table 2, samples 4, 5), but aluminum was oxidized. This follows from hydrogen release and the presence of aluminum hydroxides in the dried product according to the X-ray data. Suspensions with still higher ANP contents (H_2O : ANP = 8–25) were characterized by self-heating with intense heat release (Figure 1, Table 2, samples 9–11) and the formation of aluminum hydroxide and oxyhydroxide in substantial amounts, whereas the content of unreacted aluminum in hydrolysis products was low (Figure 2). An increase in the content of ANP to H_2O : ANP ratios of 7 and lower resulted in suspension self-heating to 100°C during aluminum oxidation. Under water deficiency conditions, powder sintering in open systems was possible, and the weight ratio H_2O : ANP = 2 calculated from the chemical reaction equation was insufficient for complete aluminum oxidation. At an H_2O : ANP ratio of 6, the oxidation of aluminum and suspension self-heating were accompanied by intense water vaporization and ANP sintering.

Table 2: Parameters of the interaction of ANP with water (v_{max} is the highest temperature growth rate, T_{max} is the highest suspension temperature, and c'_{Al} is the content of aluminum metal in hydrolysis products).



Sample	H_2O : Al (±0.5%)	v_{max}, K/s	T_{max}, °C	c'_{Al}, wt % (±0.5)
1	126	–	–	76.1
2	101	–	–	75.2
3	84	–	–	76.2
4	72	0.00	60	3.1
5	56	0.18	62	2.3
6	50	0.42	78	1.8
7	42	0.53	83	1.7
8	33	0.68	87	1.4
9	25	0.83	92	1.4
10	16	0.83	92	1.4
11	13	0.84	92	1.4
12	8	0.85	92	1.4

Note: Data on sample 2 (Table 1, 78 wt % Al in ANP) are given. For samples 1–3, no formation of H_2 bubbles was noticeable. For samples 5 and 6, the formation of H_2 bubbles was observed. With samples 6–12, hydrogen was released vigorously. The reaction with sample 13 was accompanied by water vaporization.

3 Conclusion

To summarize, we experimentally found the range H_2O: ANP weight ratios (8–25) at which the reaction occurred under optimum conditions (Figure 1, Table 2, samples 9–12) with the most complete conversion of ANP in its oxidation with liquid water (the residual content of aluminum in hydrolysis products was 1.4 wt %). We showed experimentally that the oxidation of aluminum nanopowder with liquid water in a suspension preliminarily heated to 64–66°C was characterized by an induction period (0.8 – 6.0 min) and self-heating to 92°C with heat and molecular hydrogen release.

Acknowledgement

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