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# INFLUENCE OF HOT HYDROGEN ON WATER BOILING

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*The influence of dispersion and aluminium powder content in aqueous suspension on aluminium oxidation with liquid water has been investigated. It is stated that after heating aqueous suspension of electroblasting aluminium nanopowder to 64...66 °C aluminium oxidation process is characterised by the subsequent induction period and possible suspension self-heating with heat and hydrogen evolution. It is shown that at aqueous suspension self-heating the boiling temperature does not exceed 94 °C. The mechanism of water boiling is described.*

## Introduction

At present the considerable experimental results showing that nanoparticles and nanopowders are the new state of substance characterized by properties of solid and at the same time liquid and macromolecules are cumulated [1]. Due to its structure-energy state they present the number of unusual properties [2].

It is known that each substance in liquid state boils at certain temperature and external pressure. Boiling is the process of liquid evaporation not only from open surface but also in its depth where vapor bubbles start forming. Usually there is dissolved or absorbed air in liquid or in vessel walls where it is placed. Small formed gas bubble is filled up with saturated vapor of surround liquid. Vapor elasticity in it is determined by liquid temperature. If liquid temperature is so that saturated vapor pressure in a bubble is lower than external pressure over liquid the bubble does not grow. Both hydrostatic pressure of liquid column over it and external pressure under which there is liquid prevent this.

The external pressure defines bubble equilibrium state. If external pressure is increased the bubble will shrink. If external pressure is decreased bubble volume will grow. Let external pressure does not change but temperature increases. When liquid temperature reaches the value at which the elasticity of its saturated vapor equals to external pressure the vapor pressure inside the bubble will also equal to the external one. Further temperature increase results in vapor pressure exceeding the external one inside the bubble, the latter starts growing, emerging and bursts exhausting when reaches the surface. Liquid starts evaporating not only from the surface but also from bubbles surface inside liquid: liquid is boiling. Thus, for liquid boiling it is necessary to bring its temperature to the magnitude at which the elasticity of its saturated vapors equals to the external pressure, or rather a bit higher [3].

At aluminum nanopowder (ANP) interaction with water suspension boiling is observed. Thus, molecular hydrogen and aluminum oxides-hydroxides with the developed microstructure of surface may be obtained:

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2\uparrow$$
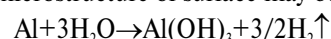
The interaction of Al with water is exothermic. Its standard enthalpy is −459,1 kJ/mole. The immediate result of heat release is water temperature rising. At certain temperature the aluminum oxidation reaction with spontaneous heating of suspension and subsequent rising the environmental (water) temperature to a boil is possible.

The aim of the given paper is to ascertain the conditions of vaporization at temperature lower than 100 °C, investigate the dependence of suspension boiling temperature on content of nanopowder and its dispersion in it.

## 1. Experimental technique

The electroblasting nanopowders of Al obtained in different conditions and industrial powder of aluminum ASD-1 were researched in the paper (Table 1).

Nanopowder denoted as NPA-M (Fig. 1, *a*) was obtained by electric blast of conductors (EBC) in the medium of gaseous argon with hydrogen admixture (10 % vol.) at excess pressure 1, 52·10⁵ Pa, charging voltage of capacitive storage 24 kV (the diameter of aluminum conductor is 0, 3 mm, the length is 75 mm). To steady electroblasting nanopowder after its obtaining the passivation at its low oxidation with air was carried out in the air [4].

Nanopowders denoted as: NPA-18, NPA-22, NPA-28 were also obtained by electric blast of conductors at the same electric parameters and charging voltage of capacitive storage, correspondingly, 18, 22, 28 kV [4].

The analysis of Al nanopowder surface microstructure showed that particles have spherical form (Fig. 1, *a*) and in this case the diameter of the most part of particles did not exceed 100 nm.

The industrial powder of aluminum ASD-1 is obtained by Al melt spraying in the medium of argon. Particles form is spherical ~100 mkm.

The parameters of chemical activity were determined by the data of thermal analysis (thermoanalyzer Q 600 of Science-analytic center of TPU). The content of metal Al was defined by volumetric method. Specific surface area was determined by the method of BET.

**Table 1.** *The parameters of aluminum powders chemical activity*

| Sample | Specific surface area $S_{sp}$, m²/g | Temperature of oxidation start $t_{os}$, °C | Referred thermal effect of oxidation $S/\Delta m$, rel. unit | Metal Al content, wt. % |
|---|---|---|---|---|
| NPA-M | 12±0,5 | 450 | 4,9 | 85,5 |
| NPA-18 | 7,7±0,25 | 550 | 2,9 | 85,7 |
| NPA-22 | 8,8±0,25 | 550 | 3,3 | 84,1 |
| NPA-28 | 9,9±0,3 | 530 | 5,5 | 85,8 |
| ASD-1 | 0,15±0,03 | 680 | 2,1 | 99,5 |

On the basis of Al powders and warm distilled water (50 °C) the samples of aqueous suspensions at mass ratio $H_2O$:Al=100:1...6:1 were prepared. Suspension constantly stirred in thermostable glass was heated to 64...66 °C (hot-type magnetic stirrer) after that suspension stirring went on without heating (magnetic stirrer without heating). Chromel-alumel thermocouple (conductors diameter is 0,3 mm) was used as a temperature sensor where temperature is recorded by electron potentiometer recorder «KSP-4».Temperature was also controlled by standard mercury thermometer with accuracy of ±0,1 °C. Temperature measurement was carried out from the beginning of suspension heating (~50 °C) to its cooling (~25 °C). After the reaction water excess was removed by the method of decantation and the products (Fig. 1, *b*) were air-dried at 25 °C. To determine phase composition of hydrothermal interaction products the difractometer Rigaku D-MAX/B was used. Roentgenogram recording was carried out with the use of $CuK_\alpha$-radiation in the range of angles $2\theta$ from 20 to 100°.
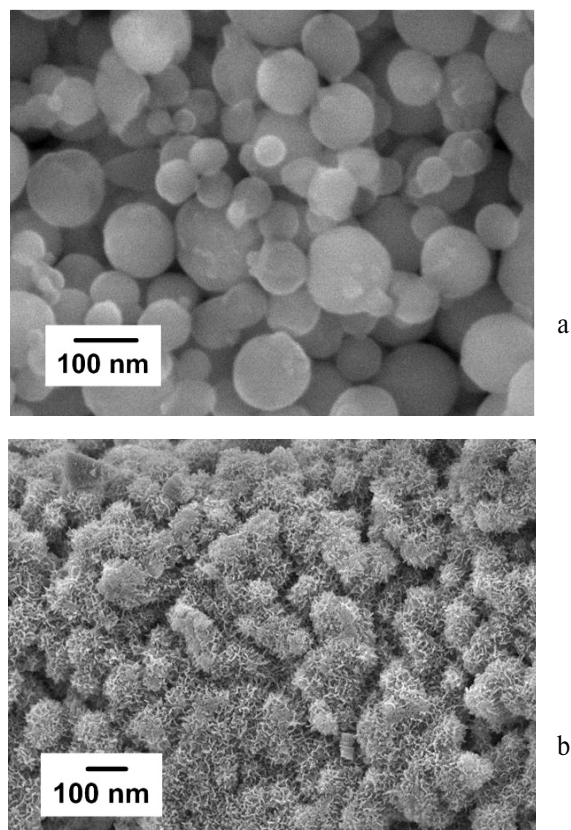




**Fig. 1.** *Micrographs of Al nanopowder: a) initial one; b) product of its interaction with water*

## 2. Discussion of the results

As a result of the experiments carrying out it was stated that thermal process was characterized by a certain induction period $\tau$ and relatively abrupt increase of suspension temperature with maximal value achieving (Fig. 2, $T_{max}$) at continuous stirring of Al nanopowder suspension heated to 64...66 °C (Fig. 2, area 1) and absence of external heating source (Fig. 2, area 2).

Maximal suspension temperature depended appreciably on aluminum nanopowder content in it (Fig. 2). On the basis of experimental data it was stated that self-heating with achieving maximal suspension temperature of 78...87 °C is typical for suspensions with Al content ($H_2O$:Al=50:1...33:1). At increasing Al content ($H_2O$:Al=8:1) self-heating with intensive heat generation (Fig. 2, Table 2, sample 4) and formation of solid products of aluminum oxidation (Fig. 1, *b*) – Al oxohydroxide and hydroxide with a very little content of aluminum is typical. The data of roentgenophase analysis

indicate it (Fig. 3) [5]. At the same time the ratio limit of NPA and water ($H_2O:Al=8:1...25:1$) at which maximal suspension temperature starts increasing due to spontaneous suspension heating with vapor formation and molecular hydrogen extraction, achieving at the end 92 °C, was recorded (Table 2, sample 4–7).
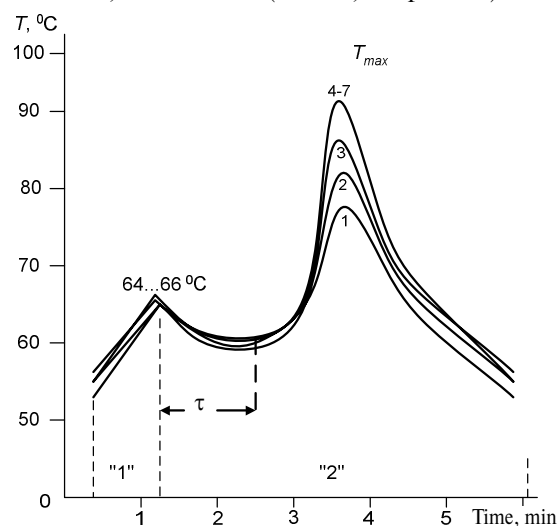


**Fig. 2.** *Temperature time change at Al nanopowder interaction with water at different ratio. Suspension stirring: «1» is with heating; «2» is without heating; $\tau_1$ is the induction period; $T_{max}$ is the maximal suspension temperature, °C; 1, 2–7 are the numbers of suspensions (Table 2)*

**Table 2.** *The parameters of the process of Al nanopowder and water interaction*

| Suspension sample | Ratio $H_2O:Al$ ($\pm0,5$wt.%) | Maximal rate of temperature rise $V_{max}$, °C/s | Maximal temperature of suspension, $T_{max}$, °C | Al° content, ($\pm0,5$wt.%) |
|---|---|---|---|---|
| 1 | 50:1 | 0,42 | 78 | 1,80 |
| 2 | 42:1 | 0,53 | 83 | 1,66 |
| 3 | 33:1 | 0,68 | 87 | 1,44 |
| 4 | 25:1 | 0,83 | 92 | 1,43 |
| 5 | 16:1 | 0,83 | 92 | 1,43 |
| 6 | 13:1 | 0,84 | 92 | 1,42 |
| 7 | 8:1 | 0,85 | 92 | 1,42 |
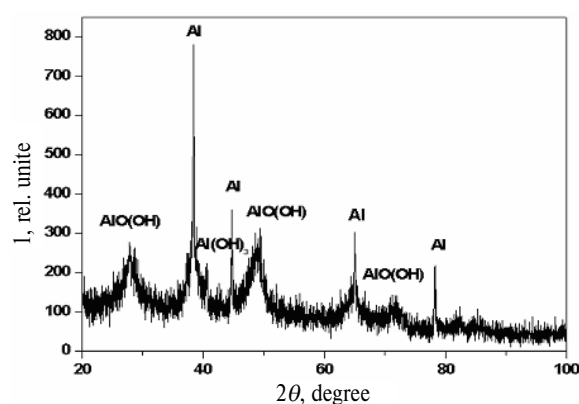


**Fig. 3.** *Typical roentgenogram of reaction product of Al nanopowder and water*

Specific surface area of aluminum powders also influenced the maximal suspension temperature. The de-

pendences of temperature time change for electroblasting Al nanopowders and industrial powder ASD-1 are presented in Fig. 4. Suspension self-heating with achieving maximal temperature equal to 82 °C (Fig. 4, *a*) is typical for ASD-1. In this case boiling was not observed. It is connected with small quantity of specific surface area (Table 1) and large diameter of particles, i.e. the impossibility of obtaining «hot» hydrogen in these conditions. The composition of reaction products indicates the absence of significant self-heating: only aluminum hydroxides are formed. In contrast to ASD-1, electroblasting Al nanopowders, having high area of specific surface and defective condition of particle surface, have high reactivity (Table 20). Maximal suspension temperature with Al nanopowder content achieves 92...94 °C (Fig. 4, *b*).
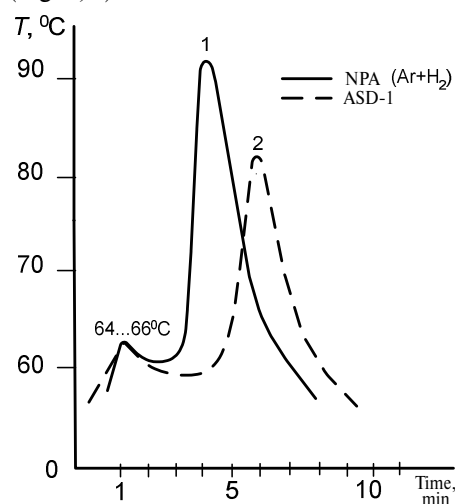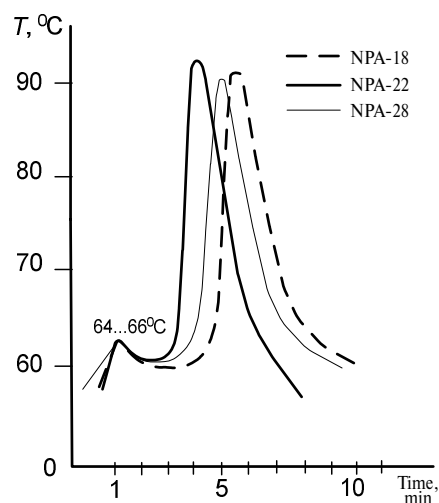


**Fig. 4.** *The time change of suspension temperature at interaction with water: a) NPA-M and ASD-1; b) NPA-18, NPA-22, NPA-28*

The connection between particle temperature $T$ and environment temperature is described within the bounds of the model supposing constant temperature value in whole particle volume, quasi-stationarity of the processes of heat- and mass transfer in particle environment and invariance of sizes of particle physical proper-

ties in process of interaction with the environment [6]. The latter supposition is true owing to the fact that for maximal temperature $T_{max}$ obtaining at self-heating the chemical conversion of some substance monolayers on particle surface is required. In contrast to more general description of metal self-heating at high temperatures the model under consideration describing self-heating at rather low temperatures (<500 °C), conforms better to nanopowders particle behavior in chosen chemical reactions. In this case the heat of chemical reaction is supposed to be the only source of self-heating.

Let us denote the thermal effect of chemical reaction as $\Delta H$. The rate of heat generation as a result of chemical reaction is equal to:

$$-\frac{dH_1}{dt} = V \cdot \Delta H \cdot U, \qquad (1)$$

where $V$ is the rate of reaction; $U$ is the volume of reacting layer (boundary layer between metal and oxide-hydroxide cover).

The rate of heat abstraction from the reacting layer through the oxide-hydroxide cover is proportional to the temperature difference in the volume of reacting layer $T$ and in the environment $T_0$:

$$\frac{dH_2}{dt} = \alpha \cdot S \cdot (T - T_0), \qquad (2)$$

where $\alpha$ is the heat-transfer coefficient of the oxide-hydroxide cover; $S$ is the surface of heat abstraction.

For self-heating realization the fulfillment of the following condition is necessary:

$$\left|\frac{dH_1}{dt}\right| > \left|\frac{dH_2}{dt}\right|,$$

Temperature increase in intermediate layer will continue to maximal temperature $T_{max}$ obtaining, i. e. to heat equilibrium fixing:

$$\left|\frac{dH_1}{dt}\right| = \left|\frac{dH_2}{dt}\right|,$$

Equating right parts of the equations (1) and (2) we obtain:

$$V\left|\Delta H\right|U = \alpha S(T_{max} - T_0),$$

whence:

$$T_{max} = V\left|\Delta H\right|\frac{U}{\alpha S} + T_0.$$

The qualitative analysis of the obtained expression shows that the value $T_{max}$ growths when reaction rate and thermal effect increasing as well as at reaction volume rising, whereas the increase of heat-transfer coefficient $\alpha$ and heat extraction surface decrease $T_{max}$. The environment temperature $T_0$ enters into the value $T_{max}$ as an additive component. It is possible to estimate the maximum available temperature $T_{max}$ by phase and chemical composition of reaction products formed in the volume of reacting layer [6].

According to the oxidation mechanism of aluminum nanoparticles with water the oxidizer is $H^+$. The oxidation process occurs on the boundary of aluminum oxide-hydroxide. Hydrogen temperature equals to the temperature in the reaction zone. Phase composition of oxidation products is the temperature test (Fig. 3, 5).

$$\begin{array}{cccc} 150\ °C & 250\ °C & 400\ °C & 700\ °C \\ Al(OH)_3 \rightarrow & \beta\text{-}Al_2O_3 \cdot 3H_2O \rightarrow & AlOOH \rightarrow & \gamma\text{-}Al_2O_3 \rightarrow \\ \text{гиббсит} & \text{байерит} & \text{бемит} & \text{тетрагональная} \end{array}$$

$$\begin{array}{ccc} & 900\ °C & 1300\ °C \\ \rightarrow & \gamma\text{-}Al_2O_3 \rightarrow & \delta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \\ & \text{псевдокубическая} & \end{array}$$

**Fig. 5.** *Sequence of aluminum hydroxide transformations when heated*

At temperature 20...25 °C the velocity of hydrogen molecules is high and at their collision with water molecules the former may increase their velocity and energy. At the same time if hydrogen molecules have high velocity they may it transfer to the water molecules. At water molecules collision with «hot» hydrogen molecules formed in the reaction zone of aluminum nanopowder with water (250...300 °C) they may get energy enough for transition into vaporous state. «Hot» hydrogen molecules may penetrate water similarly to elementary particles and form the chains of seed bubbles along its track. Water vapor and naturally vapor bubble (a stage of inception of a bubble) may be formed inside the track.

Hydrogen molecules getting the boundary of a bubble and water may promote the vaporization on bubble surface and its growth. A small formed gas bubble is filled up with saturated vapor of surrounding liquid (water). Water and gas temperature rising due to the heat of chemical reaction results in the fact that vapor pressure inside the bubble exceeds the external one, the bubble starts growing, emerging and reaching the surface releases vapor into atmosphere. Thus, boiling (vaporization) occurs at water temperature lower than 100 °C — nonequilibrium boiling due to energy transfer by «hot» hydrogen to water vapors that has been examined experimentally: water boiling at 92...94 °C.

**Conclusions**

1. It is shown that at self-heating of Al nanopowder suspensions in liquid water the boiling temperature of suspension does not exceed 94 °C. The mechanism of water boiling is described.

2. The process of Al nanopowder oxidation with liquid water in suspension, heated to 64...66 °C, is accompanied by induction period and subsequent self-heating with the extraction of molecular hydrogen.

3. Maximal suspension temperature at self-heating depends on content and dispersion of Al powders. The complete powders oxidation occurs at ratio $H_2O{:}Al=8{:}1...25{:}1$.

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# MATHEMATICAL MODEL OF DESUBLIMATION PROCESS OF VOLATILE METAL FLUORIDES

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*Mathematical model for calculation of optimal temperature desublimation in metal fluorides and the number of desublimation stages has been developed; it permits achieving the degree of base product recovery from gas-vapour mixture nearly to 100 %. Experimental checking of modeling results at uranium hexafluoride desublimation shows a good correlation with the theoretical data.*

### Introduction

Sublimation-desublimation limit, being a refining operation is of great importance in technology of obtaining a number of pure substances and semi-products including the technology of nuclear fuel.

All existing desublimators may be divided into three groups by the way of solid phase extraction from gas flow: surface, volumetric and mixed [1]. However, all these apparatus have a significant disadvantage. It is a low yield of a main product into disublimate (80...90 %), the reason of which is aerosols formation at intense overcooling of desublimated substance vapor and their carry-over from the system. In industry the desublimation processes of $ZrF_4$, $TiF_4$, $UF_6$, $WF_6$, $ReF_6$ and other volatile metal fluorides are usually carried out at temperatures, which are considerably lower than actual temperatures of desublimation. The latter cause the formation of crystallization centers in apparatus volume and as a result loss of the product in the form of aerosol.

The investigations of the influence of apparatus surface temperature on desublimation process of titanium tetrafluoride carried out before showed [2], that at desublimation temperature decrease lower than the actual one by 250 ˚C loose desublimate of pin-fin type is formed; by 150 ˚C – the layer of friable product is formed; by 100 ˚C – solid vitreous product along the whole layer is formed. In this case products output losses from desublimator were 27, 12, and 5 wt. %, correspondingly.

The most efficient way of organizing the desublimation process would be the way at which in the conditions of changing heating rate it could be possible to suppress the process of aerosols occurrence and control the desublimator layer rise ensuring apparatus maximal filling and its passability.

### 1. Aerosol formation at vapor supersaturation

The point of desublimation process is in product gaseous molecules delivery from gas-vapor mixture volume to the cold desublmator surface. As far as desublimation may occur at high rate only fulfilling the condition [1]

$$S = \frac{P}{P_{\infty(T)}} \le S_{\kappa p}, \qquad (1)$$

where $S$ is the degree of gas-vapor mixture supersaturation; $S_{cr}$ is the critical degree of supersaturation over which the formation process of solid phase nuclei in apparatus volume starts; $P$, $P_{\infty(T)}$ is the current gas pressure in the system and substance gas pressure over its desublimate at the given temperature; depending on the way of disublimation process organization various means of its behavior are possible.

If $S_{cr}$ is obtained only on the surface of disublimate then the whole product will settle on it. In this case the lower its temperature is the higher is the rate of desublimation process. However, it is stated experimentally [2] that in this case product yield into desublimate sharply decreases due to its volumetric desublimation, always occurring there where $S_{cr}$ is obtained, the zone of which will transfer from the surface into the volume of gas-vapor mixture (Fig. 1).

If we denote the input temperature of gas-vapor mixture into desublimator by $T_1$, temperature of cold surface is denoted by $T_2$, the distance which the gas-vapor mixture will cover having been cooled from temperature $T_1$ to $T_2$ is $L$ then assuming that as the distance $x$ increases from gas entry point into apparatus to its exit point the temperature of gas-vapor mixture $T$ will decrease linearly from $T_1$ to $T_2$ we obtain