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EFFECT OF PHYSICOCHEMICAL PROCESSES ON GAS GENERATION IN HEAT PIPES

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UDC 536.248.2

This paper examines the results of tests on heat pipes of various modifications. The results obtained on gas generation are compared with theory.

In the operation of heat pipes there are a number of complex physicochemical processes occurring in the working liquid, the capillary structure, and on the internal surface, and these processes result in the formation of a solid deposit and noncondensible gas (hydrogen). These products of electrochemical corrosion can appreciably alter the initial heat-pipe parameters, and in the course of time can put it out of commission. The rate of these processes varies and is determined by the nature of interaction of the heat-transfer agent with the porous wick structure and the type of wall material, and also by the thermodynamic characteristics of each of the heat-pipe elements. An increase in temperature intensifies these processes without changing their nature.

The authors have conducted comprehensive tests on heat pipes to determine the rate of formation of noncondensible gas and deposit as a function of temperature and time. The tests were conducted at elevated temperature.

The authors of [2-4] attempted to find an empirical correlation between the release of hydrogen and time and temperature, and compare it with the experimental data obtained. The objective of the present comprehensive tests is the inverse problem: to compare the experimentally obtained amount of hydrogen with the theoretical prediction [1]. The combination of heat-pipe wall material and heat-transfer agent may be varied, since the method of calculation accounts for the chemical and thermodynamic properties of both these agents.

To conduct qualitative comprehensive tests all the requirements of technical and vacuum cleanliness were observed (degreasing of the heat-pipe surface, use of chemically pure and degassed heat-transfer agents, etc.). Chromel – Copel thermocouples were used to measure the temperature drop along the entire length of the heat pipes. Only pipes for which the temperature drop $\Delta t \leq 1°C$ were used for the tests. A special vacuum fan was used to sample the noncondensible gas.

For the tests the heat pipes were mounted vertically in a special thermoelectric heater, and heat was removed from the condensation zone by natural air convection. The volume of the gas plug was determined by means of thermocouples located in the condensation zone. A qualitative analysis of the gas plug was carried

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0022-0841/79/3702-0958$07.50

TABLE 1. Heat-Pipe Variants in the Comprehensive Tests

Pipe wall material	Filler	Capillary structure
Stainless steel	Water	Stainless-steel mesh
Stainless steel	Ammonia	The same
Stainless steel	Freon-11	"
Stainless steel	Acetone	"
AMG aluminum	Water	Grooves, mesh
AMG aluminum	Ammonia	The same
AMG aluminum	Freon-11	"
AMG aluminum	Acetone	"
Copper	Water	Sintered wick
Copper	Acetone	The same
Copper	Acetone	"
Copper	Ammonia	"

out on a type KhL-69 chromatograph. For this purpose, the heat pipe, cooled in liquid nitrogen, was connected via a fan to an evacuated glass volume to serve as an intermediate container to introduce noncondensible gas into the chromatograph.

Table 1 shows a number of heat-pipe modifications subjected to tests, which showed that in heat pipes made of stainless steel, and also aluminum and its alloys, with water heat-transfer agent, there is a noticeable formation of a gas plug. But in pipes filled with acetone or ammonia, there was negligible formation of noncondensible gas. In pipes made of stainless steel and AMG alloy with Freon heat-transfer agent practically no generation of a gas plug was observed.

Figure 1a shows a chromatogram of the gas plug from a heat pipe made of type Kh18N9T stainless steel with a water heat-transfer agent. In addition to the main chromatograph background (the N_2 and O_2 peaks), one can clearly see a hydrogen peak formed from electrochemical corrosion. From the height of the peak one can evaluate the amount of component. In this case 9.2 ml of hydrogen was found in the pipe when it had operated for 800 h at temperature 180°C.

A negligible hydrogen peak was observed in chromatograms for stainless steel – acetone heat pipes (Fig. 1d) and aluminum alloy – acetone pipes (Fig. 1e). No hydrogen peak was observed in the aluminum

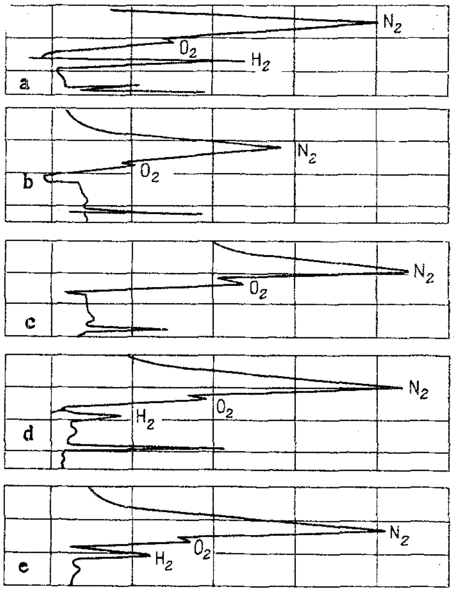

Fig. 1. Chromatograms of the gas plugs in heat pipes of various modifications: a) stainless steel – water; b) stainless steel – Freon-11; c) aluminum – Freon-11; d) aluminum – acetone; e) stainless steel – acetone.

TABLE 2. Activation Energy and the Equilibrium Potential for the Various Heat Pipes

Pipe wall material	Heat-transfer agent	ΔE_{act}, kJ/mole	Potential between heat-transfer agent and material
Stainless steel	Water	81,6	—0,44
	Ammonia	259,8	—0,26
	Acetone	118,6	—0,23
Aluminum	Water	90,5	—1,66
	Ammonia	389,5	—0,96
	Acetone	305,8	—0,85
Copper	Water	—	+0,37

alloy – Freon-11 pipes (Fig. 1c) and the stainless steel – Freon-11 pipe (Fig. 1b). The operating time of the heat pipes was 2300 h at temperature 150°C. In the aluminum alloy – water heat pipes there was the considerable hydrogen formation and solid deposition, and the pipes rapidly went out of service. In the remaining heat-pipe modifications no appreciable changes were observed.

An explanation of this phenomenon is that the process of slowing the electrochemical corrosion depends to a considerable extent on the activation energy ΔE_{act}. For a large value of ΔE_{act} the molecules do not acquire enough energy to overcome the potential barrier and form a new, more stable, thermodynamic compound (compounds of aluminum and iron with ammonia, acetone, etc.).

The activation energies were calculated from the formula

$$\Delta E_{act} = \frac{4.57 T_1 T_2}{T_2 - T_1} \lg \frac{K_2}{K_1}. \tag{1}$$

Here K_1 and K_2 are the rate constants for the process at the appropriate temperatures.

The amount of hydrogen liberated is an exponential function and takes the form

$$m_{H_2} = A\exp\left[-\left(\frac{\Delta E_{act} - B}{RT}\right)t\right]. \tag{2}$$

A detailed analysis of Eq. (2) is given in [1]. The experimentally obtained amount of hydrogen agrees quite well with the theoretical values (Table 3).

Table 2 shows the quantities necessary to calculate the gas liberated and the solid deposited in heat pipes. It can be seen from Table 2 that the lowest value of activation energy is obtained with the stainless steel – water system, and the highest value with the aluminum – ammonia system. This means that the interaction of aluminum with ammonia to form hydrogen may only occur at a temperature above critical, when the kinetic energy of the NH_3 molecules is enough to overcome the energy barrier. The stainless steel – water system interacts at temperatures of 100-150°C with appreciable formation of H_2 and $Fe(OH)_2$.

An important factor in the gas generation process is the quantity $\Delta\varphi = \Delta E_B$, i.e., the equilibrium potential between the heat-pipe wall material and the heat-transfer agent. This potential is negative for all the combinations presented in Table 2 (apart from copper – water), which means that the given metal may liberate hydrogen. Copper lies to the left of hydrogen in the order of potentials, and the electrochemical corrosion process cannot occur. In fact, in carrying out the tests (800 h at t = 180°C) we noted an increase in the gas plug in the stainless steel – water heat pipes and in the aluminum – water heat pipes, but did not observe

TABLE 3. Results of the Heat-Pipe Tests

Pipe wall material	Heat-transfer agent	Duration of test, h	Test temperature t, °C	Amount of hydrogen liberated, ml	
				calculated	experimental
Stainless steel	Water	800	180	12,2	9,2
AMG alloy	Water	1300	180	11,1	11,07
Stainless steel	Acetone	2300	150	5,63	4,09
Stainless steel	Ammonia	2300	100	3,6	—
AMG alloy	Acetone	2300	150	4,5	2,5
AMG alloy	Ammonia	2300	100	2,8	—
Stainless steel	Freon-11	2300	120	—	—
AMG alloy	Freon-11	2300	120	—	—
Copper	Water	2300	180	—	—

noncondensible gas appearing in the copper – water variant. During periodic checking in the pipes with stainless steel and water certain deviations from the expected results were noted. These deviations are associated primarily with the presence of dissolved hydrogen in the heat-transfer agent. This process may be described as follows:

$$\mathrm{Fe} + \mathrm{H_2O} + \frac{1}{2}\mathrm{O_2} = \mathrm{Fe(OH)_2}.$$

As a result of this reaction the value of the pH increases due to formation of the alkali $\mathrm{Fe(OH)_2}$. For pH = 9.6, which corresponds to a saturated solution of iron hydroxide, and with complete expenditure of oxygen from the aqueous solution, the rate of electrochemical corrosion, and therefore of gas generation, is practically zero. One may comment that, for operation of heat pipes of this variant, the hydrogen liberation process will proceed in a very nonuniform manner. Initially the gas plug increases at a considerable rate and then attenuates when the pH reaches a value on the order of 8-8.5. The hydrogen generation process must stop when all the free oxygen in the water has been expended and when a saturated $\mathrm{Fe(OH)_2}$ solution has formed. This phenomenon was noted in the work of other authors [1, 2]. The authors of [2] conducted tests with a series of stainless steel – water heat pipes. The heat-transfer agent for each pipe was prepared in a special way (deaeration and oxidation). The internal wall of the heat pipe was rendered passive. The experimental results indicate a clear dependence of the noncondensible gas formation rate on the oxygen concentration of the water and the degree of passivity of the internal surface of the heat pipe.

By analyzing the operation of stainless steel – water heat pipes we established that 9.2 ml of hydrogen was liberated in 800 h of operation. It was determined theoretically that one would expect to liberate 12.2 ml of hydrogen in this time. The difference between theory and experiment can be explained by the process of electrochemical corrosion becoming attenuated as the heat-transfer agent becomes saturated with ions and as the pH changes. In addition, one should take into account diffusion of hydrogen through the heat-pipe walls.

Thus, the heat-pipe tests have indicated that the effect of physicochemical processes occurring inside the pipe have an appreciable influence on the duration of operation.

The chromatographic analysis carried out has demonstrated that the liberation of gas in the pipe depends on the wall material and the heat-transfer agent.

The results presented here require future improvement by conducting long-term tests on heat pipes with various materials for the wall and the wick, and various heat-transfer agents.

NOTATION

ΔE_{act}, activation energy, kJ/mole; Δt, temperature drop along the heat pipe, °C; T, absolute temperature, °K; R, gas constant, kJ/mole · deg; t, time, sec; $\Delta\varphi_{\mathrm{b}}$, potential difference in the Volt series, V; K_1, K_2, rate constants in the electrochemical corrosion process; $m_{\mathrm{H_2}}$, total mass of hydrogen liberated in the heat pipe, mg; A, B, constants describing the hydrogen liberation process.

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