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DETERMINING THE FIREPROOF LIMIT FOR THE HEAT PROTECTIVE COATING OF THE GAS GENERATOR IN A HYDROGEN STORAGE AND SUPPLY SYSTEM

Yuriy Abramov
Doctor of Technical Sciences, Professor
Oleksii Basmanov
Corresponding author
Doctor of Technical Sciences, Professor, Leading Researcher
Scientific and Testing Department of Fire Protection
and Fire Extinguishing Systems Research
Scientific and Research Center of Research and Testing
Institute of Scientific Research on Civil Protection*
E-mail: basmanov_oleksii@nuczu.edu.ua
Valentina Krivtsova
Doctor of Technical Sciences, Professor
Department of Physical and Mathematical Disciplines*
Andriy Mikhayluk
PhD, Associate Professor, Senior Researcher
Yevhen Makarov
PhD, Deputy Head of Department
Department of Special Training
and Underwater Mine Clearance*
Volodymyr Abrakitov
PhD, Associate Professor**
*National University of Civil Defence of Ukraine
Onoprienka str., 8, Cherkasy, Ukraine, 18034
**Department of Occupational and Life Safety
O. M. Beketov National University of Urban Economy in Kharkiv
Chornoglazivska srt., 17, Kharkiv, Ukraine, 61172

This work considers the task to prevent fires in hydrogen storage and operation systems. The subject of the study is the properties of the heat-protective coating of the gas generator in the hydrogen storage and supply system. The fire resistance limit is used as such a property. The set of heat-protective coating and the wall of the gas generator is considered as a thermodynamic system with two inputs. The signal at one input reflects the influence of thermal factors of the fire, and the signal at the second input corresponds to the thermal state of the gas generator cavity.

A mathematical description of such a thermodynamic system has been constructed, which is represented in operator form using the integral Laplace transform. A feature of such a mathematical notation is that it includes hyperbolic functions of an irrational argument. An approximation of mathematical models of the thermodynamic system was carried out and it is shown that these models, which are transfer functions, belong to fractional-rational functions with third-order Hurwitz polynomials. The approximation accuracy is 3.8%.

An expression for the reaction of a thermodynamic system has been derived, provided that the influence of thermal factors of a fire is described by an arbitrary function of time, and the thermal state of the gas generator cavity is described by the Heaviside function. To construct this expression, the Borel theorem and auxiliary functions are used, the parameters of which are the parameters of the roots of the algebraic Hurwitz equation.

Examples of determining the fire resistance limit for the heat-protective coating of the gas generator in the hydrogen storage and supply system for the characteristic conditions of its operation are given. It is shown that the fire resistance limit of such a coating is 462.8 s at a critical temperature of 320°C under the condition that the influence of thermal factors of a fire is linear (the generalized temperature change rate is 2.0°C s^{-1}). In this case, the thermal state of the gas generator cavity is stationary and is characterized by a temperature of 60°C

Keywords: hydrogen systems, gas generator, fire, heat-protective coating, fire resistance limit, Laplace transform

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1. Introduction

Global energy challenges and environmental problems are becoming increasingly urgent while traditional energy sources such as oil, coal, and natural gas are gradually being depleted. As a result, new clean and economical energy sources are being actively developed, including hydrogen energy [1]. Being a renewable secondary energy source, hydrogen energy has several advantages, such as abundant resources, high combustion efficiency, zero pollution, and storage capability [2]. Hydrogen storage systems (HSSs) are used to store hydrogen, one of the main requirements for which is to ensure their safe operation [3]. Ensuring the required level, in particular, fire safety of HSS, can be achieved using heat-shielding coatings. To answer the question of the effectiveness of heat-shielding coatings, it is necessary to have information about their properties under the influence of thermal factors of fire. Therefore, fires in hydrogen storage and operation systems are a pressing issue.

2. Literature review and problem statement

Regarding hydrogen systems, it should be noted that they have a steady trend towards both their increase and the expansion of their areas of application. An example is the situation in transport, in particular, the market share of hydrogen fuel cell vehicles (FCEV) in North Korea increased from 0.7% in 2014 to 4.1% in 2021. The number of registered vehicles has exceeded one million [4]. In [5], intensive development of hydrogen trains is indicated, which is being carried out by CP in Canada, CRRC in China, CZ in the Czech Republic, PESA in Poland, Wabtec in the USA, and KPPI in Korea. However, as noted in [6], there are serious safety issues associated with the hydrogen process. The safety problems of hydrogen systems have two aspects – safety related to the properties of hydrogen and safety related to the operation of such systems.

The wide range of hydrogen flammability – (4÷75) vol.% [7], as well as the wide range of explosivity – (16÷59) vol.% [3] – necessitate the determination of those two parameters for specific conditions of hydrogen use. For this purpose, it is considered appropriate to use predictive estimates of hydrogen flammability and explosivity. Obtaining such estimates can be done experimentally, numerically, or analytically [8]. Experimental methods are mostly used in laboratory settings. Numerical methods require substantiation of the accuracy in determining predictive estimates. Analytical and numerical methods require confirmation of their adequacy. During HSS operation, the influence of various factors, such as material damage, design defects, personnel errors, or external collisions and impacts, can lead to the occurrence of fire and explosion hazardous events [9]. In [10] it is indicated that effective risk assessment is crucial in preventing fires and explosions in hydrogen systems. Using the method of accident risk assessment for industrial systems (ARAMIS) and computational fluid dynamics (CFD) methods on the example of HSS in the form of a gas station, risk levels were obtained that do not exceed $5.8 \cdot 10^{-5}$. However, obtaining such a quantitative risk assessment (QRA) is integral and does not provide identification of hazardous factors.

In [11], the results of the fire hazard analysis of FCEV vehicles are presented using a method that combines failure mode and effect analysis (FMEA) with a risk assessment matrix. This approach is used for qualitative analysis of the hydrogen fuel cell system of a vehicle, dividing them into subsystems or components and analyzing them one by one according to the required level of analysis. The FMEA results are qualitatively analyzed using a risk assessment matrix, which provides visualization for assessing the severity of each risk. It should be noted that the FMEA analysis is carried out without taking into account the influence of people, the environment, and the interaction between different subsystems or components.

In [12], QRAs of the latest modification of a hydrogen filling station were obtained, which was due to the improvement of the technologies of components or means used in its operation. It should be noted that when obtaining QRAs, it is necessary to take into account the frequency of these risks. This circumstance is a rather significant problem since the array of statistical data regarding such hydrogen systems is practically absent. To overcome this situation, the risk frequencies were estimated using data from chemical plants. There is no justification for such an equivalent use of statistical data. It should be noted that for the risk analysis of ECEV vehicles, all studies mainly use FMECA, FFMEA, FTA, and HAZOP methods, most of which are qualitative risk analysis based on fuzzy mathematics.

An example of using HAZOP methods in conjunction with FMEA methods is the study on an on-board hydrogen storage and delivery system, given in [13]. Four scenarios are considered: hydrogen refueling, hydrogen storage, hydrogen delivery, and pumping. It should be noted that data on the reliability of the risk assessments are not provided. In addition, it should be noted that the results of the risk assessment depend on the accuracy of the numerical models, such as hydrogen leakage, diffusion, combustion, as well as on the modeling conditions, such as grid size and boundary conditions. The influence of these factors is not considered.

Hydrogen storage cylinders are the most common way of storing hydrogen used in HFCF. Cylinders with an operating pressure of 35 MPa or 80 MPa are mainly used [14]. For example, the Toyota Mirai is equipped with two tanks with a pressure of 70 MPa ($V_1 = 60$ l and $V_2 = 62.4$ l). Paper [11] reports the results of studies on the consequences of hydrogen storage tank rupture during a fire. It has been experimentally shown that the risk of hydrogen storage tank explosion is associated with the combined contribution of physical and chemical energy of the explosion. It should be noted that studies of this type are exclusive in nature, and recommendations for the safe operation of vehicles are intuitive in nature. Work [14] reports data on the conditions under which explosions can occur but quantitative estimates of the probabilities of their occurrence are not provided.

The authors of [15] present a methodology for quantifying the risk of hydrogen tank rupture. Two scenarios of tank charge (SoC) are considered – SoC = 99% and SoC = 59%. The number of fatalities per vehicle per year, the cost of each case, and the fire resistance rating (FRR) of the hydrogen tank are used as risk indicators. The methodology of this approach to risk assessment does not make it possible to obtain information about the possibility of a fire and explosion situation. The characteristics of such a fire and explosion situation for a motor vehicle are given in [4]. It has been experimentally shown that the temperature of a fire in a car interior can reach 10^3°C, and the fire growth rate is $5.5 \cdot 10^{-3}$ kW·s^{-2}, assuming the concept of t-quadratic fire growth curve.

Paper [16] reports the results of the spread of fire to neighboring HFCV vehicles equipped with thermal pressure relief devices (TPRD). In the case of a HFCV fire and when TPRD is activated, a fireball with a diameter of more than 10 m is formed. Such studies are exclusive and costly, and their results, if replicated, require correction. It is characteristic of studies of this type that they make it possible to obtain information about the conditions under which fires can occur in hydrogen systems. But the question of the probability of their occurrence is open. One way out of this situation is to establish a connection between fire safety indicators and reliability indicators.

An example of such an approach is the result of the study given in [17], in which the probability of failure-free operation of its main elements is used to determine the probability of occurrence of a combustible environment in HSS. The peculiarity of such an approach is that data on the reliability indicators of HSS are practically absent. First of all, this applies to such a promising class of HSS as solid-state systems [18]. A way out of this situation may be associated with the use of non-traditional methods for obtaining estimates of reliability indicators. In [19], to obtain the reliability indicators of a gas generator of a hydrogen storage and supply system, its frequency characteristics are used – amplitude-frequency and phase-frequency characteristics. The limitations of such an approach are due to the fact that the estimates of the reliability indicators of a gas generator of a hydrogen storage and supply system are determined only at the time of its launch.

In [20], the reliability indicator of a gas generator of a hydrogen storage and supply system – the probability of failure-free operation – is determined using its amplitude-frequency characteristic. It should be noted that this approach to determining reliability indicators is multi-stage, as a result of which errors occur at each stage of its implementation, the values of which are integrated. This drawback is absent if the dependence of pressure on operating time at a random point in time is used to determine the level of fire hazard of a gas generator of a hydrogen storage and supply system through its reliability indicator [21]. The probability of trouble-free operation of a gas generator of a hydrogen storage and supply system is determined using the Laplace function, the argument of which is the rate of change of pressure in its cavity. The value of this parameter depends on several factors, in particular the temperature, which is not controlled.

It should be noted that all options for determining reliability indicators given in [29–21] relate to the gas generator as a functional element of the hydrogen storage and supply system. The use of these indicators to obtain estimates of the reliability indicators of the entire system requires justification. One of the ways to achieve such justification is to use the control of the fire-hazardous state of the hydrogen storage and supply system. In [22], such control is provided by the fire safety subsystem of the hydrogen storage and supply system. The presence of such a fire safety subsystem opens up the possibility of restoring the fire-hazardous state of the hydrogen storage and supply system. Such an option is possible based on the results of control and testing of the hydrogen storage and supply system. It should be noted that the algorithm for restoring the fire-hazardous state of the hydrogen storage and supply system, and its implementation are not considered.

In [2], a different approach is considered to reduce risks during the operation of a hydrogen storage and supply system based on metal hydrides. It has been shown that the heat released during the exothermic absorption process can cause the temperature of the metal hydride to increase. This can lead to thermal instability, a decrease in the hydrogen absorption rate, and a reduction in cycle time. Similarly, the heat absorbed during the endothermic desorption process can cause a temperature drop. This can negatively affect the kinetics of hydrogen absorption or release. Therefore, effective temperature control techniques are crucial for improving the performance and safety of metal hydride-based hydrogen storage and delivery systems.

In [13], possibilities for improving the performance and safety of hydrogen storage and supply systems based on hydro reactive compositions are substantiated. These possibilities are based on controlling the temperature or pressure in the cavity of the gas generator of the hydrogen storage and supply system. Examples of technical implementation of such an approach are given. It should be noted that the results of the studies reported in [22, 24] apply only to solid-state hydrogen storage and supply systems – based on metal hydrides and based on hydro reactive compositions. Regarding hydrogen storage and supply systems of other types, appropriate studies are required. In [9, 15], when analyzing risk in hydrogen systems, the fire resistance index (limit) is used as a risk indicator. Such studies are an example of solving a classical analysis problem, which results in the absence of algorithms for selecting methods and means that ensure risk reduction (if necessary) in a hydrogen system. One way out of this situation is to use heat-shielding coatings – thermal protection systems (TPSs) [24]. The most significant results in this direction have been obtained in the rocket and space industry.

In [25], a review of research in this area is presented using the example of using TPS sandwich structures for hypersonic vehicles, which includes 119 sources of information. TPSs of this type are focused on protection against thermal effects at heat fluxes at the level of 100 $W \cdot cm^{-2}$ and temperatures at the level of (1800÷1900) K. Numerical, analytical, and experimental methods and their combinations are used to determine the characteristics of TPSs, in particular, the fire resistance limits.

In 2013, the UN introduced the GTR#13 fire resistance test protocol, which lists standard fire resistance tests. However, as practice shows, the reproducibility of GTR#13 is difficult to achieve, especially when a new HSS design is in place [26]. This circumstance necessitates the study of more acceptable and reliable methods for ensuring the safety of hydrogen systems. One of the directions is the use of experimental methods. However, experiments require a large open area, are very expensive, and often cannot provide an idea of the heat transfer mechanism. To save expensive investments in experimental studies, attention is focused on simulation studies. These studies include the use of numerical methods that are implemented using application software packages. An example of such an approach using a 3D fire safety model of a hydrogen system that combines ANSYS FLUENT and ANSYS Mechanical is given in [26]. Regarding numerical research methods, it should be noted that the results obtained with their help depend on the size of the grid. In addition, these methods do not always provide for analytical analysis of the research results. In particular, numerical methods for studying hydrogen systems have limited capabilities in terms of reflecting the influence of all factors, assessing their significance, and highlighting the main ones.

In [27], analytical methods of research on heat-shielding coatings and heat-shielding screens are reported. These methods are based on the use of the Laplace integral transform when finding a solution to the differential equation of heat conductivity. The specificity of this approach is that the solution to the differential equation of heat conductivity, which is given in operator form, includes hyperbolic functions of irrational complex argument. This circumstance causes significant mathematical difficulties in the transition from the image to the original of the function, which is the solution to the differential equation of heat conductivity. The degree of these difficulties increases with the complexity of the boundary conditions.

Our review provides grounds for conducting research aimed at devising methods and means for reducing risks during the operation of hydrogen storage and supply systems. One of such research areas is determining the fire resistance limit of the heat-shielding coating of the gas generator in a hydrogen storage and supply system.

3. The aim and objectives of the study

The purpose of our study is to determine the fire resistance limit of the heat-protective coating of the gas generator in a hydrogen storage and supply system as a functional element of the thermodynamic system. In practice, this opens up opportunities for obtaining express estimates of the properties of heat-protective coatings of gas generators in the hydrogen storage and supply system.

To achieve this goal, it is necessary to solve the following problems:

– to provide a mathematical description of the thermodynamic system, the functional element of which is the heat-protective coating of the gas generator in a hydrogen storage and supply system, under the condition of the influence of thermal factors of fire on it;

– to build mathematical models that formalize the reactions of the thermodynamic system to thermal effects, and provide examples of their use in determining the fire resistance limit of the heat-protective coating of the gas generator;

– to provide a generalized algorithm for determining the fire resistance limit of the heat-protective coating of the gas generator.

4. The study materials and methods

The object of our study is a gas generator in a hydrogen storage and supply system. The subject of the study is the properties of the heat-shielding coating of the gas generator in a hydrogen storage and supply system. The principal hypothesis of the study assumes that the heat-shielding coating of the gas generator and its wall are considered as a thermodynamic system, the formalization of thermal processes in which is carried out using the integral Laplace transform.

The basic assumption is that the transfer functions of the thermodynamic system, which take into account the influence of thermal factors of the fire and the thermal state of the gas generator cavity, are approximated by fractional-rational functions of a complex argument.

The integral Laplace transform is used to describe the thermal state of the heat-shielding coating of the gas generator in a hydrogen storage and supply system. When determining the reaction of the thermodynamic system to thermal influences, its impulse transition function, Borel's theorem, and methods of the theory of the function of a complex variable are used. Dynastic brick or fireclay brick are used as the material of the heat-shielding coating of the gas generator. The wall of the gas generator is made of composite material.

5. Results of research on determining the fire resistance limit of the heat-protective coating of the gas generator

5. 1. Mathematical description of a thermodynamic system with a heat-insulating coating

The totality of the heat-protective coating with a thickness of h_1 and the wall of the gas generator of the hydrogen storage and supply system with a thickness of h_2, on which this heat-protective coating is applied, represent the thermodynamic system "heat-protective coating – wall". From the side of the heat-protective coating, the influence of fire factors in the form of heat flux q and temperature T_1 takes place. In the cavity of the gas generator, there is temperature T_2.

Thermal processes in the heat-protective coating of the gas generator are described by the differential equation

$$\frac{\partial\theta(x,t)}{\partial t}=a\frac{\partial^2(x,t)}{\partial x^2}, \tag{1}$$

where $\theta(x, t) = T(x, t) - T_0$; $T(x, t)$ – current temperature in the heat-shielding coating; $T_0 = T(x, 0)$; a – thermal conductivity coefficient of the heat-shielding coating; x – coordinate; t – time.

The boundary and initial conditions take the form:

$$-\lambda\frac{\partial\theta(0,t)}{\partial x}=q-\alpha_1\left[\theta(0,t)-\theta_1\right]; \tag{2}$$

$$\theta(h_1,t)=\omega(t); \tag{3}$$

$$-\lambda\frac{\partial\theta(h_1,t)}{\partial x}=c_{s2}\frac{d\omega(t)}{dt}+\alpha_2\left[\omega(t)-\theta_2\right]; \tag{4}$$

$$\theta(x,0)=0, \tag{5}$$

where λ is the coefficient of thermal conductivity; α_1 is the coefficient of convection heat transfer from the heat-shielding coating to the environment; c_{s2} is the specific surface heat capacity of the gas generator wall; α_2 is the coefficient of convection heat transfer from the free surface of the gas generator wall

$$\theta_1=T_1-T_0;\ \ \theta_2=T_2-T_0. \tag{6}$$

If we take into account

$$\tau_0=a^{-1}h_1^2;\ \ a=\lambda c_{v1};\ \ c_{vi}=c_{si}h_i,$$

$$C=c_{v2}c_{v1}^{-1};\ \ Bi_i=\alpha_i h_1\lambda^{-1},\ \ i=1,\,2, \tag{7}$$

where τ_0 is the characteristic time of heating of the heat-shielding coating; c_{vi} is the specific volumetric heat capacity ($i = 1$ – heat-shielding coating; $i = 2$ – gas generator walls); c_{s1} is the specific surface heat capacity of the heat-shielding coating; Bi_i is the i-th Bio criterion, we represent the solution to the differential equation (1) using the integral Laplace transform in the form

$$\begin{aligned}\theta(x,p)&=L\left[\theta(x,t)\right]=\\&=A(p)\exp(kx)+B(p)\exp(-kx),\end{aligned} \tag{8}$$

where L is the Laplace integral transform operator; p is a complex variable; $k = (a^{-1}p)^{0.5}$; $A(p)$, $B(p)$ are functions to be defined, then for the function $\omega(t)$ after using (3) to (5) we have

$$\begin{aligned}\omega(p)&=L\left[\omega(t)\right]=\\&=\left[\theta_{1m}Bi_1+Bi_2\begin{pmatrix}\mathrm{ch}\left(\tau_0p\right)^{0.5}+\\+Bi_1\mathrm{sh}\left(\left(\tau_0p\right)^{0.5}\right)\left(\tau_0p\right)^{-0.5}\end{pmatrix}\theta_2\right]\times\\&\times\left[p\begin{bmatrix}\left(Bi_1Bi_2+\tau_0p\left(1+CBi_2\right)\right)\times\\\times\mathrm{sh}\left(\left(\tau_0p\right)^{0.5}\right)\left(\tau_0p\right)^{-0.5}+\\+\left(Bi_1+Bi_2+C\tau_0p\right)\mathrm{ch}\left(\tau_0p\right)^{0.5}\end{bmatrix}\right]^{-1},\end{aligned} \tag{9}$$

where

$$\theta_{1m}=q\alpha_1+\theta_1. \tag{10}$$

Expression (9) describes the temperature change in the heat-shielding coating due to the action of two factors, which are formalized by the parameters θ_{1m} and θ_2. Expression (9) can also be interpreted as the reaction $\omega(t)$ of the thermodynamic system to the input signals $x_1(t) = \theta_{1m}$ and $x_2(t) = \theta_2$.

With this approach, the thermodynamic system will correspond to the structural-dynamic scheme shown in Fig. 1.

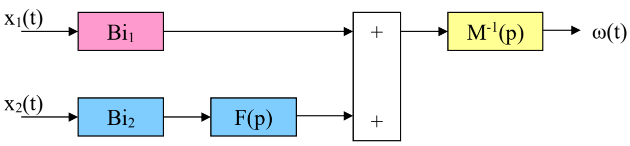

Fig. 1. Structural-dynamic diagram of a thermodynamic system

The functions $F(p)$ and $M(p)$ are described by the following expressions

$$F\left(p\right)=\mathrm{ch}\left(\tau_0 p\right)^{0.5}+Bi_1\mathrm{sh}\left(\left(\tau_0 p\right)^{0.5}\right)\left(\tau_0 p\right)^{-0.5}; \tag{11}$$

$$M\left(p\right)=Bi_1Bi_2+\tau_0 p\left(1+CBi_2\right)\mathrm{sh}\left(\left(\tau_0 p\right)^{0.5}\right)\left(\tau_0 p\right)^{-0.5}+$$
$$+\left(Bi_1+Bi_2+C\tau_0 p\right)\mathrm{ch}\left(\tau_0 p\right)^{0.5}. \tag{12}$$

A feature of this structural-dynamic scheme is that it has two inputs. The first input contains the signal $x_1(t)$, which reflects the influence of the thermal factors of the fire on the heat-protective coating. The second input of the structural-dynamic scheme contains the signal $x_2(t)$, which corresponds to the thermal state of the gas generator cavity. The reaction of such a thermodynamic system to signals $x_i(t)$ is determined by the following expression

$$\omega\left(t\right)=\sum_{i=1}^{2}\omega_i\left(t\right), \tag{13}$$

where the i-th additive component takes the form

$$\omega_i\left(t\right)=L^{-1}\left[W_i\left(p\right)L\left[x_i\left(t\right)\right]\right]. \tag{14}$$

In this expression, L^{-1} is the inverse Laplace transform operator; $W(p)$ is the transfer function of the thermodynamic system at the i-th input. For these transfer functions, there are expressions

$$W_1\left(p\right)=Bi_1M^{-1}\left(p\right);\;\; W_2\left(p\right)=Bi_2F\left(p\right)M^{-1}\left(p\right). \tag{15}$$

It should be noted that the peculiarities of transfer functions (15) are the presence of hyperbolic functions of irrational argument in their composition. This circumstance complicates their practical use. One way out of this situation is to approximate the transfer functions $W_i(p)$ by fractional-rational functions.

Under the condition of polynomial approximation of hyperbolic functions

$$\mathrm{ch}\left(\tau_0 p\right)^{0.5}=\sum_{i=0}^{2}f_ip^i;\;\; \mathrm{sh}\left(\left(\tau_0 p\right)^{0.5}\right)\left(\tau_0 p\right)^{-0.5}=\sum_{i=0}^{2}d_ip^i, \tag{16}$$

where f_i, d_i are the approximation parameters, the transfer functions (15) will be transformed to the form:

$$W_1\left(p\right)=Bi_1\left[\sum_{i=0}^{3}b_ip^i\right]^{-1}=Bi_1\left[b_3\prod_{n=1}^{3}\left(p-p_n\right)\right]^{-1}; \tag{17}$$

$$W_2\left(p\right)=Bi_2\left[\sum_{k=0}^{2}a_kp^k\right]\left[\sum_{i=0}^{3}b_ip^i\right]^{-1}=$$
$$=Bi_2\left[\sum_{k=0}^{2}a_kp^k\right]\left[b_3\prod_{n=1}^{3}\left(p-p_n\right)\right]^{-1}, \tag{18}$$

where p_n – roots of the algebraic Hurwitz equation

$$\sum_{i=0}^{3}b_ip^i=0. \tag{19}$$

The parameters b_i and a_k are defined by the expressions:

$$b_0=Bi_1+Bi_2+Bi_1Bi_2;$$

$$b_1=C\tau_0+Bi_1Bi_2d_1+\left(1+CBi_1\right)\tau_0+\left(Bi_1+Bi_2\right)f_1;$$

$$b_2=C\tau_0f_1+Bi_1Bi_2d_2+\left(1+CBi_1\right)\tau_0d_1+\left(Bi_1+Bi_2\right)f_2;$$

$$b_3=C\tau_0f_2+\left(1+CBi_1\right)\tau_0d_2; \tag{20}$$

$$a_0=1+Bi_1;$$

$$a_1=f_1+Bi_1d_1;$$

$$a_2=f_2+Bi_1d_2.$$

The algorithm for determining the transfer functions of the thermodynamic system $W_1(p)$ and $W_2(p)$ is reduced to the implementation of the following options:

– formation of an array of initial data – α_1, α_2, c_{s1}, c_{s2}, h_1, h_2, λ, a;

– determination of the values of the parameters Bi_1, Bi_2, τ_0 and C;

– determination of the values of the approximation parameters f_i, d_i;

– determination of the values of the parameters of polynomials a_k, b_i;

– finding roots p_n of the algebraic Hurwitz equation (19).

Example 1. If $Bi_1=0.2$; $Bi_2=0.3$; $C=2{,}0$; $\tau_0=9{,}0$ s, then the value of variable p belongs to the range (0÷1.0) s^{-1}. In this case

f_1=4.21 s; f_2=4.78 s^2; d_1=1.48 s; d_2=0.81 s^2,

as a result, the approximation error of functions $\mathrm{ch}(\tau_0 p)^{0.5}$ and $\mathrm{sh}((\tau_0 p)^{0.5})(\tau_0 p)^{-0.5}$ does not exceed 1.7% and 1.5%, respectively. The values of parameters (20) are equal to

b_0=0.56; b_1=33.1 c; b_2=97.2 c^2;

b_3=90.1 c^3; a_0=1.2; a_1=4.5 c; a_2=4.9 c^2.

For such parameter values, the relative deviation error between the transfer functions $M(p)$ and

$$b_3\prod_{n=1}^{3}\left(p-p_n\right)$$

does not exceed 5.7% with an average value that does not exceed 3.8%.

The roots of the algebraic Hurwitz equation (19) are

$$p_1=-0.02\,\mathrm{s}^{-1};$$

$$p_2=\left(-0.53+j0.26\right)\mathrm{s}^{-1};$$

$$p_3=\left(-0.53-j0.26\right)\mathrm{s}^{-1},$$

where j – imaginary unit.

5. 2. Mathematical models of the reaction of a thermodynamic system to thermal influence

In the general case, the thermal influence on a thermodynamic system is described by the expressions

$$x_1(t)=m(t);$$

$$x_2(t)=\theta_2\cdot 1(t), \qquad (21)$$

where 1(t) is the Heaviside function; θ_2 = const.

For components $\omega_i(t)$ of the reaction of this system to the influence (21) we have:

$$\omega_1(t)=Bi_1 b_3^{-1}L^{-1}\left[W_0(p)L\left[m(t)\right]\right]; \qquad (22)$$

$$\omega_2(t)=Bi_2\theta_2 b_3^{-1}L^{-1}\left[p^{-1}W_0(p)\sum_{k=0}^{2}a_k p^k\right], \qquad (23)$$

where

$$W_0(p)=\left[\prod_{n=1}^{3}(p-p_n)\right]^{-1}=L\left[w_0(t)\right]. \qquad (24)$$

The function $w_0(t)$, which is an impulse transition function, is defined by the expression

$$w_0(t)=L^{-1}\left[W_0(p)\right]=\begin{bmatrix}(p_3-p_2)\exp(p_1t)+\\+(p_1-p_3)\exp(p_2t)+\\+(p_2-p_1)\exp(p_3t)\end{bmatrix}\times$$
$$\times\left[(p_1-p_2)(p_1-p_3)(p_3-p_2)\right]^{-1}. \qquad (25)$$

If

$$p_1=-\sigma;\quad p_2=-\alpha+j\beta;\quad p_3=-\alpha-j\beta, \qquad (26)$$

then taking into account the ratios:

$$\phi=\operatorname{arctg}\left[\beta(\alpha-\sigma)^{-1}\right]; \qquad (27)$$

$$\exp\left[j(\beta t+\phi)\right]-\exp\left[-j(\beta t+\phi)\right]=$$
$$=2j\sin(\beta t+\phi), \qquad (28)$$

expression (25) transforms as follows

$$w_0(t)=\left[(\alpha-\sigma)^2+\beta^2\right]^{-1}\mu_1(t), \qquad (29)$$

where

$$\mu_1(t)=\exp(-\sigma t)-\left[(\alpha-\sigma)^2+\beta^2\right]^{0.5}\times$$
$$\times\beta^{-1}\exp(-\alpha t)\sin(\beta t+\phi). \qquad (30)$$

When using Borel's theorem, expressions (22) and (23) take the form:

$$\omega_1(t)=Bi_1 b_3^{-1}\int_0^t m(t-\tau)w_0(\tau)\mathrm{d}\tau=$$
$$=Bi_1\left[b_3\left[(\alpha-\sigma)^2+\beta^2\right]\right]^{-1}\int_0^t m(t-\tau)\mu_1(\tau)\mathrm{d}\tau; \qquad (31)$$

$$\omega_2(t)=Bi_2\theta_2 b_3^{-1}\left[a_2\frac{dw_0(t)}{dt}+a_1w_0(t)+a_0\int_0^t w_0(\tau)\mathrm{d}\tau\right]=$$
$$=Bi_2\theta_2\left[b_3\sigma\left[(\alpha-\sigma)^2+\beta^2\right]\right]^{-1}\times$$
$$\times\left[a_2\sigma^2\mu_2(t)+a_1\sigma\mu_1(t)+a_0\mu_0(t)\right], \qquad (32)$$

where:

$$\mu_0(t)=1-\exp(-\sigma t)-\sigma\left[(\alpha-\sigma)^2+\beta^2\right]^{0.5}\times$$
$$\times\left[\beta(\alpha^2+\beta^2)\right]^{-1}\begin{bmatrix}\exp(-\alpha t)\begin{bmatrix}\beta\cos(\beta t+\phi)+\\+\alpha\sin(\beta t+\phi)\end{bmatrix}-\\-(\beta\cos\phi+\alpha\sin\phi)\end{bmatrix}; \qquad (33)$$

$$\mu_2(t)=-\begin{bmatrix}\exp(-\sigma t)+\left[(\alpha-\sigma)^2+\beta^2\right]^{0.5}\times\\\times(\sigma\beta)^{-1}\exp(-\alpha t)\begin{bmatrix}\beta\cos(\beta t+\phi)-\\-\alpha\sin(\beta t+\phi)\end{bmatrix}\end{bmatrix}. \qquad (34)$$

The fire resistance limit t_v of the heat-protective coating of the gas generator in a hydrogen storage and supply system is determined by the root of the transcendental equation

$$\omega(t)-\omega_v=0, \qquad (35)$$

where ω_v is the critical temperature value.

Example 2. The function $x_1(t)$, which reflects the influence of thermal factors of fire on the thermodynamic system, takes the form

$$x_1(t)=\theta_{1m}\cdot 1(t). \qquad (36)$$

In this case, expression (31) takes the following form

$$\omega_1(t)=Bi_1\theta_{1m}b_3^{-1}\int_0^t w_0(\tau)\mathrm{d}\tau=$$
$$=Bi_1\theta_{1m}\left[b_3\sigma\left[(\alpha-\sigma)^2+\beta^2\right]\right]^{-1}\mu_0(t). \qquad (37)$$

Fig. 2 shows graphical dependences $\omega_1(t)$, $\omega_2(t)$ and $\omega(t)$ at $\theta_{1m}=10^3$°C [4] and $\theta_2=60$°C [23] using data from Example 1.

For $\omega_v=320$°C the fire resistance limit of the heat-protective coating is 77.2 s.

It should be noted that during the operation of hydrogen storage and supply systems, a passive mode of operation of the gas generator may occur, for which $\theta_2=0$ can be assumed. In this case, $\omega(t)=\omega_1(t)$, and the fire resistance limit of the heat-protective coating is 107.1 s.

Example 3. For the initial phase of the fire, function $x_1(t)$ is approximated by the following expression

$$x_1(t)=a_{1m}t, \qquad (38)$$

where a_{1m} is the generalized rate of temperature change.

In this case, expression (31) takes the following form

$$\omega_1(t)=Bi_1a_{1m}b_3^{-1}\int_0^t(t-\tau)w_0(\tau)\mathrm{d}\tau=$$
$$=Bi_1a_{1m}\left[b_3\sigma\left[(\alpha-\sigma)^2+\beta^2\right]\right]^{-1}\left[t\mu_0(t)+\mu_{11}(t)\right], \qquad (39)$$

where

$$\mu_{11}(t)=t\sigma^{-1}\left[1-\exp(-\sigma t)\right]+$$
$$+\sigma\left[(\alpha-\sigma)^2+\beta^2\right]^{0.5}\left[\beta\left(\alpha^2+\beta^2\right)\right]^{-1}\times$$
$$\times\left[\begin{array}{l}\exp(-\alpha t)\left[t\left[\alpha\sin(\beta t+\phi)-\beta\cos(\beta t+\phi)\right]\right]-\\ -\left(\alpha^2+\beta^2\right)^{-1}\left[\begin{array}{l}\left(\alpha^2-\beta^2\right)\sin(\beta t+\phi)-\\ -2\alpha\beta\cos(\beta t+\phi)\end{array}\right]\end{array}\right]+$$
$$+\left(\alpha^2+\beta^2\right)^{-1}\left[\left(\alpha^2-\beta^2\right)\sin\phi-2\alpha\beta\cos\phi\right]. \quad (40)$$

Fig. 3 shows graphical dependences $\omega_1(t)$, $\omega_2(t)$ and $\omega(t)$ at $a_{1m}=2.0°C\cdot s^{-1}$ using data from Examples 1, 2.

For $\omega_v=320°C$, the fire resistance limit in this case is 462.8 s.

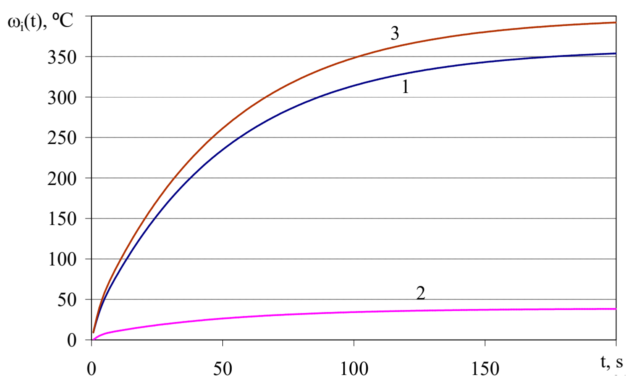

Fig. 2. Dependence of the temperature of the heat-shielding coating on time: 1 – $\omega_1(t)$; 2 – $\omega_2(t)$; 3 – $\omega(t)$

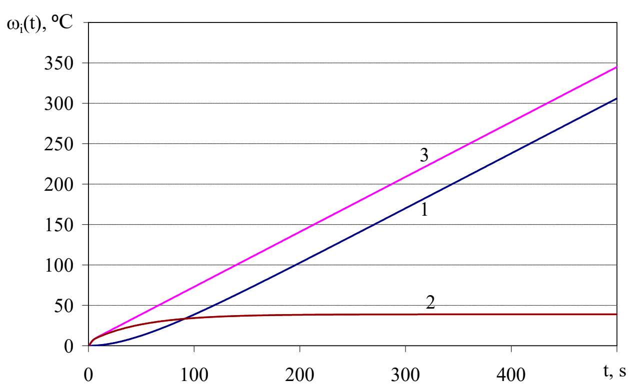

Fig. 3. Dependence of the temperature of the heat-shielding coating on time: 1 – $\omega_1(t)$; 2 – $\omega_2(t)$; 3 – $\omega(t)$

5. 3. Generalized algorithm for determining the fire resistance limit of the heat-shielding coating of a gas generator

The results obtained regarding the transfer function of the thermodynamic system, as well as mathematical models of the system's response to thermal shock, formalize the procedure for obtaining estimates of the fire resistance limit of the heat-shielding coating of the gas generator in a hydrogen storage and supply system. This, in turn, makes it possible to develop an algorithm that can be represented in verbal form as follows:

– determine the transfer functions of the thermodynamic system $W_1(p)$ and $W_2(p)$ with parameters b_i and a_k;

– know roots p_n in the algebraic Hurwitz equation – expression (19);

– determine the auxiliary functions $\mu_i(t)$, $i=0..2$ – expressions (30), (33), and (34);

– use Borel's theorem to determine the reaction of the thermodynamic system $\omega_1(t)$ to the influence of thermal factors of fire – expression (31);

– determine the reaction of the thermodynamic system $\omega_2(t)$ to the thermal state of the gas generator cavity – expression (32);

– find the root of transcendental equation (35).

The transfer functions of the thermodynamic system $W_1(p)$ and $W_2(p)$ with parameters b_i and a_k are determined using the algorithm given in chapter 5. 1.

6. Discussion of results based on research into determining the fire resistance limit of the heat-protective coating of a gas generator

The use of a heat-protective coating of the main functional element of the hydrogen storage and supply system is one of the ways to increase its level of fire and explosion safety. To determine the properties of such a heat-protective coating under the influence of thermal factors of a fire, a non-stationary heat conductivity equation with the corresponding boundary and initial conditions (2) to (5) is used. The reaction of the heat-protective coating of the gas generator of the hydrogen storage and supply system to the thermal influence of fire factors, taking into account the thermal state of the gas generator, is determined by the temperature of such a coating. For the temperature of the surface of the heat-protective coating, which is in contact with the wall of the gas generator, using the integral Laplace transform, an expression in the operator form (9) was obtained. The derived expression is interpreted as the reaction of the thermodynamic system "heat-protective coating – wall of the gas generator" to the influence of thermal factors of a fire and to the thermal state of the gas generator cavity. This approach opens up the possibility of constructing a structural-dynamic scheme of such a thermodynamic system. A feature of such a structural-dynamic scheme is that it has two inputs, to which the corresponding signals are supplied. One of these signals describes the influence of thermal factors of the fire, and the second – the thermal state of the gas generator cavity. The properties of such a thermodynamic system are described by transfer functions for each of its inputs (15).

The peculiarities of such transfer functions are that they include hyperbolic functions of irrational complex argument. To simplify the structure of transfer functions, polynomial approximation of hyperbolic functions (16) is used. As a result, such transfer functions are represented by fractional-rational functions of complex argument. With this approach, the minimum order of the Hurwitz algebraic equation (19) does not exceed three. An example of such an approach to the description of transfer functions of a thermodynamic system shows that with approximation errors of hyperbolic functions, the values of which do not exceed 1.7%, the average error of the difference between transfer functions does not exceed 3.8%. Using transfer functions of a thermodynamic system in the form of fractional-rational functions, expressions (17), (18), makes it possible to determine the reaction of such a system in the form of a superposition of two functions. This definition is based on the use of the impulse transition function (25), which is defined through the roots of the algebraic Hurwitz equation. As a result, the components of the response of a thermodynamic system to thermal action are determined using the Borel theorem and auxiliary functions (30), (33), and (34).

This makes it possible to determine the reaction of the thermodynamic system for the general case of the influence of thermal factors of fires, that is, this approach is universal. The fire resistance limit of the heat-protective coating is reduced to finding the root of transcendental equation (35). It should be noted that the obtained mathematical models are a formalization of the reactions of the thermodynamic system to typical influences of thermal factors of fire. These models are included as components in the algorithm for obtaining express estimates of the fire resistance limit of the heat-protective coating of the gas generator of the hydrogen storage and supply system. As typical influences of thermal factors of fire, influences described by the Heaviside function and the linear function of time are used.

The advantage of the above approach to determining the fire resistance limit of the heat-protective coating of the gas generator in a hydrogen storage and supply system relative to known achievements [26, 27] is the possibility of distributing proven methods of technical cybernetics for the analysis of dynamic systems. In addition, the mathematical restrictions that occur in [27] when using the inverse Laplace transform for functions that include hyperbolic functions of irrational argument are removed.

The positive aspects of using the above approach for determining the fire resistance limit of the heat-shielding coating of the gas generator of the hydrogen storage and supply system include simplicity and a high degree of efficiency. This is due to the fact that the transfer functions of the thermodynamic system are determined a priori, and determining the fire resistance limit of the heat-shielding coating of the gas generator is reduced to finding a solution to transcendental equation (35) using the Borel theorem. This, in turn, makes it possible to obtain prompt predictive estimates of the fire resistance limit of the heat-shielding coating of the gas generator of the hydrogen storage and supply system.

The limitations in determining the fire resistance limit of the heat-protective coating of the gas generator in a hydrogen storage and supply system are due to the assumption regarding the type of transfer functions of this system. In particular, this assumption leads to the fact that the order of the Hurwitz polynomial cannot be less than three.

The disadvantage of the procedure for determining the fire resistance limit of the heat-protective coating of the gas generator is that it applies to linear thermodynamic systems "heat-protective coating – wall".

Further development of this area of research may be associated with determining the fire resistance limit of the heat-protective coating of the gas generator in a hydrogen storage and supply system under the condition of a random nature of the change in thermal impact.

7. Conclusions

1. A mathematical description of thermal processes in the heat-shielding coating of the gas generator of the hydrogen storage and supply system under the influence of thermal factors of a fire has been provided. Such a mathematical description is represented in operator form using the integral Laplace transform. It is shown that such a mathematical notation corresponds to the structural-dynamic scheme of the thermodynamic system, the functional element of which is the heat-shielding coating of the gas generator. At the first input, a signal acts that reflects the influence of thermal factors of a fire, and at the second input there is a signal that corresponds to the thermal state of the gas generator cavity. This approach makes it possible to represent a mathematical model of the thermodynamic system in the form of two transfer functions. A feature of these transfer functions is the presence in their composition of hyperbolic functions of an irrational argument of a complex variable. It is shown that polynomial approximation of hyperbolic functions transforms the transfer functions of the thermodynamic system to a fractional-rational form with third-order Hurwitz polynomials. An algorithm for constructing transfer functions of a thermodynamic system is presented and an example of its implementation is given. It is shown that the average approximation error of transfer functions does not exceed 3.8%.

2. The thermal effect on a thermodynamic system is considered under the condition that the thermal effect of fire factors is described by an arbitrary function, and the thermal state of the gas generator cavity is described by the Heaviside function. It is shown that the reaction of the thermodynamic system to such an effect is determined using the impulse transfer function of the system. Expressions for auxiliary functions have been obtained, the parameters of which are the roots of the algebraic Hurwitz equation, and which are components of the functions describing the reaction of the thermodynamic system to thermal effects. The formalization of the reaction of the thermodynamic system to the action of thermal factors of fire is carried out using the Borel theorem. To determine the fire resistance limit of the heat-protective coating of the gas generator, a transcendental equation is used, which reflects the reaction of the thermodynamic system to thermal effects. The example shows that at a generalized fire temperature $\theta_{1m} = 10^{3}$°C, and a temperature characterizing the thermal state of the gas generator cavity $\theta_2 = 60$°C, for a critical temperature $\omega_\nu = 320$°C the fire resistance limit of the heat-protective coating is 77.2 s. For the initial phase of the fire at a generalized temperature change rate $a_{1m} = 2{,}0$°C·s^{-1} and at $\theta_2 = 60$°C the fire resistance limit of the heat-protective coating of the gas generator is 462.8 s.

3. A generalized algorithm for determining the fire resistance limit of a heat-protective coating of a gas generator has been provided in verbal form. The algorithm includes determining the transfer functions of the thermodynamic system and finding the roots of the algebraic Hurwitz equation. This makes it possible to formalize the reaction of the thermodynamic system to thermal effects and find the root of the transcendental equation that determines the fire resistance limit.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

The data will be provided upon reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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