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Thermodynamic Study of Fire-Protective Material

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Abstract. The paper considers the material for the protective coating of building structures made of wood. The possibility of chemical processes occurring in the material leading to its expansion has been studied. The coefficient of expansion of the material when heated is practically established. It has been established that the material can swell, both under the influence of flame and when the temperature rises at a low speed. Swelling coefficient at the same time it reaches 8. The temperature range of swelling is 150–250 °C, which is confirmed by thermodynamic calculations and experimentally. The temperature at which the material begins to swell is lower than the temperature of thermal destruction of wood.

Introduction

Currently, natural building materials such as wood are still used. The use of such building structures [1,2] is possible with the provision of fire safety measures.

In scientific works [3,4], fire safety of buildings and structures, methods of analyzing the development of combustion of a room [5,6] were previously considered. Development of protective equipment [7,8], coatings [9,10], plasters [11].

Unresolved issues

Organic coatings have a high swelling coefficient [12], which provides high heat capacity and low thermal conductivity. However, organic compounds are capable of thermal decomposition with the release of hazardous substances [13,14]. The complexity of organic production [15,16] entails a high cost of the material. Also, the production of organic substances is not environmentally friendly [17,18]. The expansion of some organic materials upon heating [19,20] determines their use for fire protection at the present time. An inorganic substance capable of swelling is liquid glass.

An important component of the study of a chemical system [21,22] is the calculation of thermodynamic characteristics [23,24]. Thermodynamic studies are widely used to study various kinds of systems, including silicate ones. Thus, when obtaining the temperature dependence of the change in the Gibbs energy (onwards ΔG) of the system under study, one can judge the possibility of a chemical reaction proceeding in the forward or reverse direction in the investigated temperature range. At temperatures that correspond to positive ΔG values, a forward reaction is impossible.

Main part

While studying a material based on a xerogel using chemical thermodynamics, we can determine the possibility of a particular process, the energy effect, theoretically predict the possibility of processes occurring when the coating is heated. The chemical process that takes place in the coating material when heated is described using the equation:

$$H_4SiO_4 + Na_2CO_3 \leftrightarrow Na_2SiO_3 + CO_2\uparrow + 2H_2O\uparrow \quad (1)$$

The calculation of ΔG was carried out for the reaction of chemical transformation in a hard coating upon heating, using the thermodynamic characteristics of substances (Table 1). In this case, it was taken into account that when the xerogel is heated, the carbonate decomposes with the release of a gaseous component, which contributes to an increase in the volume of the coating.

Table 1. Standard thermodynamic values of substances

Substance	Enthalpy, [kJ·mol $^{-1}$]	Enthalpy, [kJ·mol $^{-1}$]	ΔG, [kJ·mol $^{-1}$]	Equation coefficients, C_p, [kJ·mol $^{-1}$·K $^{-1}$]		
				a	$b \cdot 10^3$	$c \cdot 10^{-5}$
H_4SiO_4	-1481.14	200.18	-1333.86	215.06	–	–
Na_2CO_3	-1131.00	136.40	-1048.50	11.02	244.20	-4.98
Na_2SiO_3	-1556.70	113.80	-1469.67	130.29	40.17	-27.1
CO_2	-393.51	138.07	-394.38	44.14	9.04	-8.54
H_2O gas	-241.82	188.72	-228.61	30.54	10.29	–
H_2O liquid	-285.83	69.91	-237.18	52.93	47.61	7.24

An increase in temperature during a fire leads to the initiation of processes that reduce the temperature of the surface of the structure. Thermodynamic calculations make it possible to estimate the probability of these processes occurring when the temperature changes.

Calculation of ΔG for chemical reaction (1) for the temperature range was carried out according to the method:

$$\Delta H_r^0 = \sum \Delta H_{pr}^0 - \sum \Delta H_{sm}^0 , \tag{2}$$

where ΔH_r^0 – change in the enthalpy of the system due to the reaction, [kJ·mol $^{-1}$];
$\sum \Delta H_{pr}^0$ – the sum of the standard enthalpies of formation of the reaction products, [kJ·mol $^{-1}$];
$\sum \Delta H_{sm}^0$ – the sum of the standard enthalpies of formation of the starting materials of the reaction, [kJ · mol $^{-1}$];

$$\Delta G_r^0 = \sum \Delta G_{pr}^0 - \sum \Delta G_{sm}^0 ; \tag{3}$$

$$\Delta a = \sum a_{pr} - \sum a_{sm} ; \tag{4}$$

$$\Delta b = \sum b_{pr} - \sum b_{sm} ; \tag{5}$$

$$\Delta c = \sum c_{pr} - \sum c_{sm} , \tag{6}$$

where a, b, c – coefficients in the equations of the dependence of the heat capacity of the initial substances and products on temperature.

$$\Delta H^0 = \Delta H_{p298}^0 - \Delta a \cdot 298 - 0.5 \cdot \Delta b \cdot 298^2 + \Delta c \cdot 298^{-1} ; \tag{7}$$

$$\Delta G_T^0 = \Delta H^0 - \Delta a \cdot T \cdot \ln T - 0.5 \cdot \Delta b \cdot T^2 - 0.5 \cdot \Delta c \cdot T^{-1} + y \cdot T , \tag{8}$$

where ΔH^0 – first constant of integration;
ΔG_T^0 – the Gibbs energy of the system at a given temperature, [kJ·mol $^{-1}$];
T – set temperature, [K];
y – the second constant of integration, which at T = 298 K, is found by the equation:

$$y = \frac{\Delta G_T^0 - \left(\Delta H^0 - \Delta a \cdot T \cdot \ln T - 0.5 \cdot \Delta b \cdot T^2 - 0.5 \cdot \Delta c \cdot T^{-1}\right)}{T}. \quad (9)$$

The values of ΔG for the investigated temperature range are presented in Table 2.

Table 2. Gibbs energy of the reaction with increasing temperature

T, [K]	298	373	473	573	673	773	873	973	1073
ΔG, [kJ·mol^{-1}]	61.1	32.9	-1.54	-33.4	-63.1	-91.0	-117.0	-141.0	-164.0

Plotting the temperature dependence of the ΔG process during heating (Fig. 1), it can be noted that at temperatures above 470 K, the substances in the coating can react with each other with the release of gas, which contributes to the swelling of the coating and an increase in its fire retardant properties. The calculation method carried out a thermodynamic study of the processes occurring under the influence of high. It was found that at a temperature of the onset of thermal destruction of wood ~ 200 °C and higher, it becomes possible for the processes of swelling of the coating to occur.

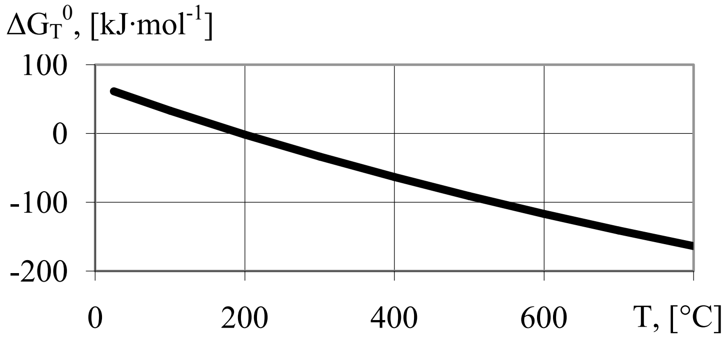

Fig. 1. Dependence of the Gibbs Energy of the system on temperature

Petrography showed the presence of a vitreous substance consisting of small vitrified particles with a size of 3–5 μm, combined into porous aggregates up to 40–50 μm in size (Fig. 2). The pore diameter in the aggregates is 5–10 μm. The pores between the aggregates are 60–80 μm in size. Rarer are individual large pores 150–300 μm in size.

Fig. 2. General view of the expanded xerogel

Fig. 2 shows a cut of the coating after exposure to heat. Under a microscope, it can be seen that the pores present in the coating are subdivided into three groups according to their size: small, regular spherical in size up to 3–5 microns, medium and large. Apparently, the formation of the smallest pores is associated with the release of carbon dioxide during the reaction with silicic acid and potassium carbonate. This reaction proceeds rather slowly due to the limited amount of silicic acid released during the hydrolysis of sodium silicate; therefore, a pronounced coalescence of gas bubbles in the gel mixture is not observed. The average pore size is apparently formed when physical water is removed from the mixture, which is located in the voids between large gel globules. Large pores are formed due to the coalescence of medium-sized pores during heat treatment.

As seen in Fig. 2, the swelling of the material does not lead to its destruction. Vitrified silica gel particles form a dense bonding layer with a wood surface without chips. The introduction of vermiculite and asbestos into the gel does not violate the integrity of the coating.

It can be concluded that the sequential passage of these reactions ensures controlled gas evolution during heat treatment of the mixture and thereby ensures swelling and material integrity.

Coating samples 70×70×3 [mm^3] were placed in a muffle furnace under normal conditions.
When the muffle furnace was turned on, the heating rate was 20 °C·min^{-1}. The samples were removed from the muffle furnace with an increase in temperature by every 50 °C.

It was found that material swelling occurs in the temperature range 150–250 °C (Fig. 3).

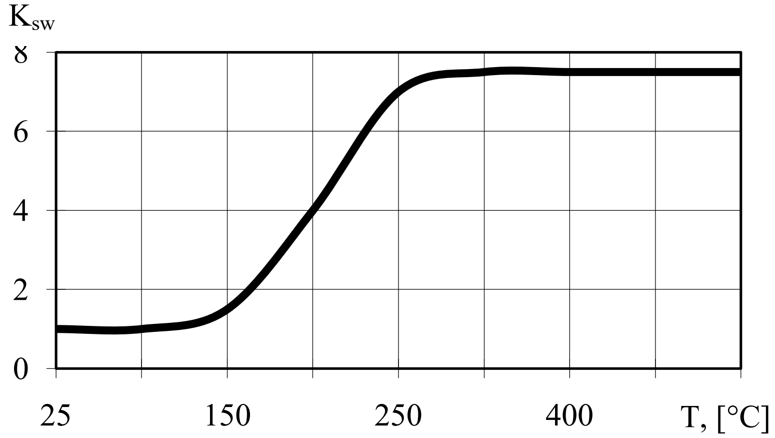

Fig. 3. Dependence of the swelling coefficient K_{sw} from temperature (at a heating rate of 20 K·min^{-1})

A significant decrease in the swelling coefficient for a material at a low heating intensity has been experimentally proven. It can be seen from the given dependence that the Gibbs energy decreases with increasing temperature. The swelling coefficient of the material was experimentally established at a low heating intensity of more than 7.

Conclusion

It has been established that the material can swell, both under the influence of flame and when the temperature rises at a low speed. Swelling coefficient K_{sw}. at the same time it reaches 8. The temperature range of swelling is 150–250 °C, which is confirmed by thermodynamic calculations and experimentally. The temperature at which the material begins to swell is lower than the temperature of thermal destruction of wood.

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