Journal of Engineering Physics and Thermophysics, Vol. 73, No. 1, 2000

THERMAL PROTECTION BASED ON CRYSTALLINE HYDRATES

A. K. Alekseev and M. P. Shuvalov

UDC 536.5:519.6

Consideration is given to the possibility of using crystalline hydrates as a source of water, on whose evaporation most of the heat passing to the protected surface is expended. A version of the thermal protection based on silica fabric, whose pores are partly filled with a crystalline hydrate, is studied. Test results are presented. Experimental data are analyzed.

The chemical inertness and environmental purity of water vapor and the large heat of vaporation render water attractive for use as a component of thermal protection (TP) that absorbs heat both in the evaporation and filtration of a gas through a porous structure. Calculations demonstrate that a thermal protection consisting of a layer of highly porous material with an emitting outer surface, an air gap, and a layer of water-saturated porous material on the protected surface is much lighter and thinner than the best samples of traditional passive TP (for example, plate thermal protection of the Space Shuttle). However, a significant shortcoming of such TP is that it is difficult to avoid premature evaporation of the water, especially at low pressures.

Attempts at using water in thermal protective materials have been made more than once [1-3]. The proposed TP versions can be divided into two types according to the method of water storage. In TP of the first type, the water-saturated layer is placed on the outside of the protected surface, and in TP of the second type, on the inside. A TP version of the first type was mentioned for the first time in [1]. Polymer microcapsules were proposed for water storage. However, their tightness was not achieved even in ground tests. Great successes were attained by Bobrov and Kuryachii [2, 3]. Bobrov and Kuryachii [2] considered the capabilities of systems with an internal layer of water-impregnated capillary-porous material. Evaporation occurs in the internal cavity with a single hole. Water passes to the heating zone by capillaries. It was shown that, in the case of high-rate heating, the vapor-air mixture formed can reject the liquid from the protected wall and expel it to the internal cavity. The premature drying of a porous protective layer can cause the superheating of the structure. Study [3] examined versions of arranging the protective layer on the outside of the protected surface. The impegnation of this layer due to capillary wetting from a leakproof vessel is carried out on opening special holes. It was shown that the thickness of such combined TP in the ideal case can be decreased by about a factor of six and the mass by more than half in comparison with passive TP. However, the reliability of this scheme is not evident.

The current study proposes to place, in the protective layer, crystalline hydrates (CH) or a CH-filled highly porous material produced after the impregnation and drying. The water mass in CH can amount to 50% and more. It is proposed to locate the CH layer on the outside of the protected wall behind the thermal protection, since in this case heat is expended additionally in superheating the vapor-air mixture during its filtration through the porous outer layer. All other things being equal, the saturated vapor pressure above CH is markedly lower than that above the water surface, which should ease the problem of keeping this TP intact until the beginning of operation. Of course, under vacuum conditions the crystalline hydrate layer (CHL) still has to be stored in a leakproof vessel, but in this case the mass of this shell can also be smaller because it is subjected to smaller loads. Thermal protection based on CH (TPCH) can consist both of several layers of a porous material and a CH layer, and of a single CHL (which can be used, for example, as a fire-extinguishing means). The latter, more simple TPCH version was chosen for testing.

S. P. Korolev Space-Rocket Corporation "Energiya," Korolev, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 73, No. 1, pp. 75-79, January–February, 2000. Original article submitted January 11, 1999.

1062-0125/2000/7301-0073$25.00 ©2000 Kluwer Academic/Plenum Publishers

TABLE 1. Basic Characteristics of Experimental Specimens

Specimen No.	Thickness, mm	Presence of foil	Initial mass M_0, g	Final mass M_f, g	$\Delta M/M_0$
1	3	–	45.53	33.7	0.26
2	3	–	56.4	42.1	0.254
3	3	–	51.1	38.5	0.248
4	5	–	69.9	52.3	0.25
5	5	–	92.6	65.9	0.288
6	5	+	89.5	65.6	0.26
7	10	–	158.6	110.38	0.307
8	10	+	173.3	123.2	0.295
9	10	–	144.3	98.5	0.324
10	10	+	169.6	111.7	0.34
11	10	–	162.8	111.0	0.32

Thermal protective material (TPM) is based on a package of several layers of silica texturized fabric (STF), which are broached with silica thread of the same diameter as that in the fabric. The number of ~ 1 mm-thick fabric layers varied between three and ten. The dimensions of specimens were 100 x 150 mm. The impregnation was carried out by immersion in a 90% solution of $MgSO_4.7H_2O$ CH in distilled water followed by drying under normal conditions.

In experiments, the specimens were heated on the outside by quartz lamps. For reducing the radiant component in heat transfer, in some specimens the STF layers were interleaved with nickel foil with a high reflectivity. The foil was perforated to provide the flow of the gas and the liquid between the layers (additional perforation appeared in broaching the layers into a package).

The lateral and inner sides of the package were insulated by an unimpregnated fabric. The temperature of the outer and inner surfaces of the specimens was measured with Chromel–Alumel thermocouples with wires 0.2 mm in diameter. Before and after the experiments the specimens were weighed. Experimental data are tabulated.

Figure 1 shows in what manner the temperatures of the outer and inner sides of specimens of thickness of 3, 5, and 10 mm, changed during the experiments.

The spread in the experimental data is caused by instability of the properties of the initial specimens and their testing modes. A characteristic feature of all experiments was a certain distention of the specimens and precipitation of $MgSO_4$ salt. This indicates that a part of the water, produced from CH in heating, moves via the fabric pores in the form of a salt solution. The mechanism of formation of the latter can be approximated as follows. Water vapor from the zone of CH decomposition moves in both directions by the action of a pressure drop. In a colder region, vapor condenses. The water formed moves via capillaries, dissolving both the CH and $MgSO_4$ salt. Thus, an equilibrium mixture of CH with its aqueous salt solution is formed in each material layer. The mixture composition depends on many factors (the gas and water permeability of TPM, the method and rate of heating, etc.); therefore its calculation, needed for determining the vapor pressure and the heat of evaporation, presents a certain difficulty. In numerical modeling, CH and water were assumed to be individual noninteracting phases. In this case, a heat balance in the material can be calculated:

1) the saturated-vapor pressure and the heat of vaporation of water from the CH solution were taken to be the same as for pure water and calculated from the Pitzer equation using the data of [4],

2) under the assumption that the CH decomposition follows the scheme

$$MgSO_4 \,.\, 7H_2O \rightarrow MgSO_4 + 7H_2O \,,$$

the equilibrium pressure of water vapor above CH is $P_v = K^{1/7}$ and the equilibrium constant at any temperature is found from well-known [4, 5] standard properties of materials at $T_0 = 298$ K

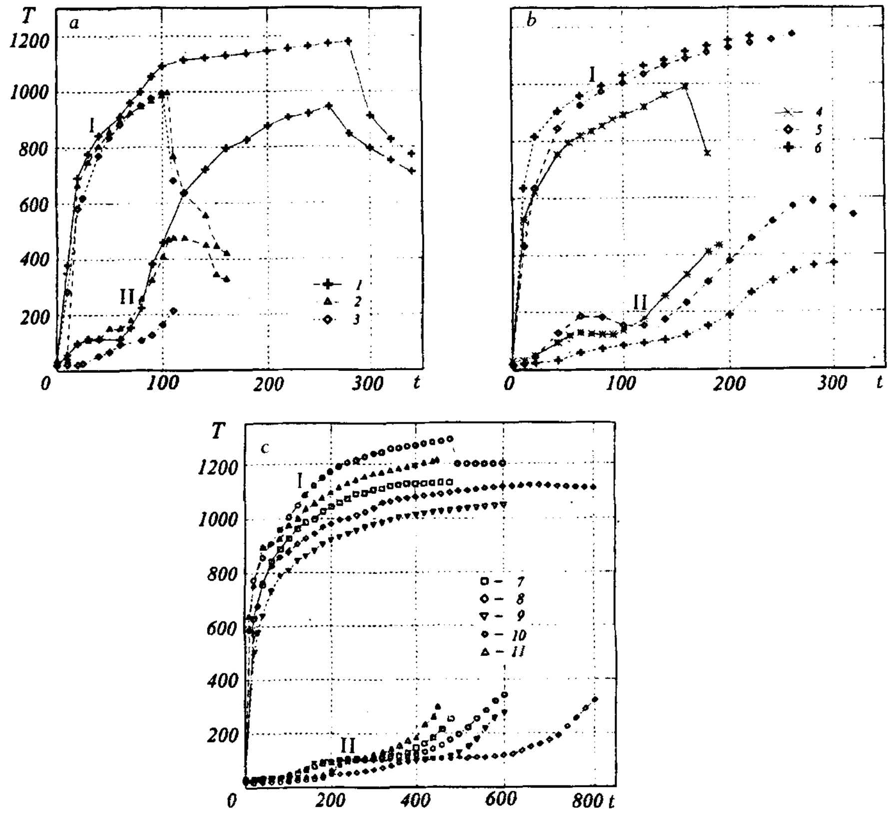


Fig. 1. Time variation of the temperatures of the outer (I) and inner (II) surfaces of specimens of thicknesses of 3 (a), 5 (b), and 10 mm (c). Numbers in the figures correspond to experiment numbers in the table. T, °C; t, sec.

$$\ln K(T) = \ln K(T_0) - \frac{\Delta H^0(T_0)}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where

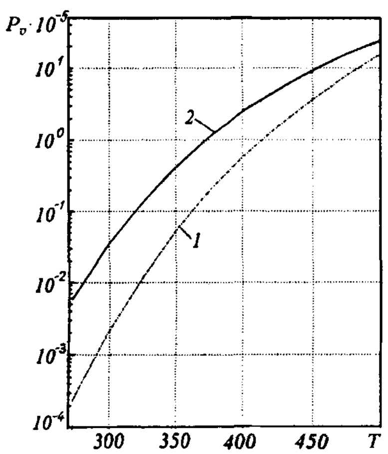
$$\ln K(T_0) = -\frac{\Delta G^0}{RT}; \quad \Delta G^0 = 7\Delta G^0_{H_2O} + \Delta G^0_{MgSO_4} - \Delta G^0_{MgSO_4 \cdot 7H_2O};$$

$$\Delta H^0 = 7\Delta H^0_{H_2O} + \Delta H^0_{MgSO_4} - \Delta H^0_{MgSO_4 \cdot 7H_2O}.$$

Figure 2 plots relations for the saturated vapor pressure above the CH and water surfaces. The vapor pressure above CH attains atmospheric pressure at $T \sim 415$ K. Assuming that in each TPM layer the vapor pressure corresponds to the equilibrium pressure and the pressure drop in the package is insignificant, it is possible to conclude that, before drying, the layer temperature must be of the order of 370–420 K. The lower limit corresponds to the case of evaporation of pure water and the upper limit, to CH decomposition without formation of a liquid phase.

The heat of decomposition of CH, calculated from the relation

$$\Delta H^0(T) = \Delta H^0(T_0) + \int_{T_0}^{T} \Delta C_p^0(T)\, dT,$$



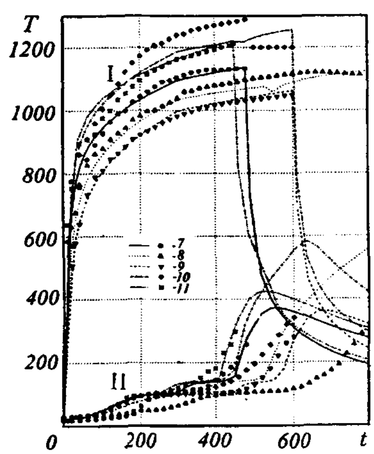


Fig. 2. Temperature dependence for the equilibrium vapor pressure above the surfaces of crystalline hydrate (1) and water (2). P_v, Pa; T, K.

Fig. 3. Calculated (curves) and experimental (dots) temperature dependences for the outer (I) and inner (II) surfaces of specimens of thickness 10 mm. T, °C.

under the condition of equal specific heats

$$C^0_{pH_2O} = 33.58 \text{ J/(mole} \cdot \text{K)}, \quad C^0_{pMgSO_4} = 96.48 \text{ J/(mole} \cdot \text{K)},$$

$$C^0_{pMgSO_4 \cdot 7H_2O} = 372.0 \text{ J/(mole} \cdot \text{K)}$$

in the temperature range of 293–420 K varies slightly from 389 to 384 kJ/mole. If the heat of evaporation of water at 373 K is 40.66 kJ/mole, then the formation of 1 mole of vapor from CH at the same temperature already requires about 55 kJ.

The calculation was carried out in a one-dimensional formulation using the procedure of study [6]. The water-vapor diffusion in a porous structure was taken into account. The thermophysical properties (effective thermal conductivity and total heat) of a multicomponent system needed for determining the TPCH heating were calculated using Dul'nev's procedure [7]. Water, CH, precipitated $MgSO_4$ salt, water vapor, and STF were considered as components. The data on the densities and specific heats of the components were borrowed from [5, 8, 9]. Radiant energy transfer in material was calculated in the approximation of an optically thick layer.

Change in specimen size during an experiment was not modeled; it was assumed that the final thickness of a specimen is equal to the initial thickness. Furthermore, the motion of the liquid phase was not modeled in the calculations.

Figure 3 presents results calculated for the heating of 10 mm-thick specimens. The temperature dependences for the specimens without foil (Nos. 7, 9, and 11) are in good agreement. The presence of foil (specimens Nos. 8 and 10) gives rise to additional factors that were disregarded in the calculations: contact resistance between the fabric and the metal and variation in the gas permeability of the package (because of possible gas spreading along the foil, the problem ceases to be one-dimensional).

NOTATION

P, pressure; T, temperature; t, time; M, ΔM, mass and its variation; K, equilibrium constant of the reaction with respect to partial pressures; C^0_p, standard molar specific heat at constant pressure; ΔH^0, standard molar enthalpy of formation; ΔG^0, Gibbs standard molar energy of formation.

REFERENCES

1. B. A. Shvedov, *Energy and Mass Transfer in Thermal Protective Materials for Space-Rocket Systems*, Doctoral Dissertation in the Physical-Mathematical Sciences, Moscow (1990).
2. I. N. Bobrov and A. P. Kuryachii, *Teplofiz. Vys. Temp.*, **30**, No. 2, 351-358 (1992).
3. A. P. Kuryachii, *Izv. Ross. Akad. Nauk, Mekh. Zhidk. Gaza*, No. 1, 24-36 (1995).
4. R. Reed, J. Prausnitz, and T. Sherwood, *Properties of Gases and Liquids* [Russian translation], Leningrad (1982).
5. V. A. Rabinovich and Z. Ya. Khavin, *Concise Chemical Reference Book* [in Russian], Leningrad (1978).
6. M. P. Shuvalov, in: *Proc. 3rd Minsk Int. Forum "Heat and Mass Transfer–MIF-96,"* Minsk, May 20-24, 1996 [in Russian], Vol. 3, Minsk (1996), pp. 205-209.
7. G. N. Dul'nev and V. V. Novikov, *Transfer Processes in Heterogeneous Media* [in Russian], Leningrad (1991).
8. A. Misnar, *Thermal Conductivity of Solids, Liquids, Gases, and Their Compositions* [Russian translation], Moscow (1968).
9. G. N. Dul'nev and Yu. P. Zarichnyak, *Thermal Conductivity of Mixtures and Composite Materials* [in Russian], Leningrad (1974).