Theory and practice for the manufacture of a composite thermal heat shield for a space ship

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Abstract. The technological processes were explored for the manufacture in an autoclave of a space ship heat shield. A mathematical model was created for the determination of the duration of the impregnation of the binder for the composite material. The change in the Nitrogen content is dependent on the time in the autoclave. This dependence relates to the use of the minimum amount of electricity to reduce the expense of the process in practice.

1. Introduction
The development of manned space flight is impossible without solving problems of thermal protection of spaceships and crew during their return to Earth. When entering the dense atmosphere at a rate of 8-12 km/s, the pressure and the temperature on the surface of the descending spaceship (DS) from the side of forward flow reaches high values in the process of adiabatic compression. The duration of landing and the rise of heat flow are sufficient for the destruction of any of the known materials, therefore, in DS a special windshield with ablative thermal protection is used [1-6].

Figure 1. The layout of heat strata within the material of the thermal protection: 1 – DS metal wall; 2 – basic material layer of thermal-protective coating (TPC); 3 – pyrolysis binder layer (separation of liquid and gas phase) and formation of charred residue; 4 –“sacrificial” erosion layer; \( Q \) – heat flow, \( U_\infty \) – spaceship speed, \( T_{\text{max}} \), \( P_{\text{max}} \) – maximum temperature and pressure occurring during adiabatic compression of air flow at the stagnation point.
The effect of ablative thermal protection is schematically represented in figure 1. Intense heat flow $Q$ causes the formation of several areas in heat-protective material. In area 2, in the direction from design wall 1, the DS material serves as a thermal shield, thus, it must have low thermal conductivity (coefficient of thermal conductivity ≤ 0.2 W/m K).

The intense power loads have an influence on the material of thermal protection. The material with minimum porosity and compositional structure, including filler and matrix (binder after polymerization) is used. The fibrous filler is a package of woven workpieces sewn in thickness on the base of asbestos, basalt, quartz or kaolin fibers.

In area 3, at high temperature the process of matrix high-molecular polymer decomposition occur with the formation of volatile decomposition products and coke residue. The part of incoming heat is consumed for an endothermic reaction process of polymer transformation. Coke performs a function of an absolute black body in the process of radial heat flux in accordance with Stefan-Boltzmann law. Matrixes of ablative thermal protection type on the basis of phenol-formaldehyde and silicone thermosetting binder are the most effective in relation to the process of coke formation (coke output is up to 65%).

In area 4, at temperature of more than 2000-2500 K the gaseous, liquid and solid phases, which are carried away by the atmospheric incoming air flow, are separated from glowing coke that maintains strength. It is a so-called “sacrificial” layer of DS thermal protection, which is exposed to erosive carry-over. The requirements for the reduction of the thermal protection cover are thickness $U_{\text{carry over}} \leq 0.1$ mm/s.

This paper is dedicated to a discussion of the technological features for the provision of DS thermal protection requirements and the prospects for further improvement of the technological processes.

2. Manufacture of a thermal protective coating for a descending spaceship

The production technology of a thermal protection cover for reusable spaceships was developed by the Rocket-Space Corporation “Energy” (RSCE) named after S P Korolyov, which is currently the only organization in Russia that holds and develops the technologies for spaceships and man-controlled space flight.

[Image: DS thermal protective shell (a) and frontal heat shield (b).]

The development of thermal protection (figure 2) ensured the high aerodynamic quality and reliability of the descending spaceship “Soyuz”. Invaluable experience was gained from the thermal protection of the descent vehicle “Zond” thermal protection, designed for manned flights to the Moon.
and overcoming the Earth’s atmosphere during the return with the velocity 11km/s. The results of experimental and theoretical studies were summarized in joint works of RSCE and Bauman Moscow State Technical University (BMSTU) specialists [7-23], including the application of an autoclave to cure and form the composite under the action of heated nitrogen pressure.

The required porosity of the TPC is achieved by means of repeated filling of a porous workpiece with binder and drying. Repeated filling is needed because of the secondary porosity which is formed by the evaporation of alcohol in the binder.

Figure 3. Schematic diagram of apparatus for DS thermal-protective coating impregnating under pressure:
1 – workpiece, 2 – manufacturing jig, 3 – vacuum line, 4 – vacuum pump, 5 – compressed gas bottle, 6 – the binder container, 7 – the pipeline for supplying the binder, 8 and 9 – valves, 10 – binder indicator, 11 – binder collector, 12 – valve.

The technological scheme of filling of a semi-finished product with the binder is shown in figure 3. The workpiece, 1, to be impregnated is placed in the cavity of manufacturing jig, 2, which is connected by a vacuum line, 3, with a vacuum pump, 4. As a result, vacuum in the pore space of the workpiece is produced. Following this, the compressed gas in the bottle, 5, creates in container, 6, with binder the overpressure of displacement. The binder is supplied over pipeline, 7, into pore space of the workpiece when valve, 8, is opened. In order to prevent movement of the binder in the excess binder collector, 11, the valve, 9, is closed. The impregnation process lasts until indicator, 10, shows a complete filling of the pore space with binder. Then, the vacuum pump stops working, valve, 12, is opened ensuring air drainage to the vacuum created in the special capacity of the plant. Then valve, 8, is closed and valve, 9, is opened. The bleed-out from collector 11 drains into binder container 6.

The second operation of the repeated process chain, which is carried out in an electrovacuum chamber furnace or autoclave, is a thermal vacuum drying at a temperature of $T_{\text{dry}} = 50 - 60$ °C and pressure $P_{\text{dry}} = 10 - 20$ kPa during $\tau_{\text{dry}} = 8 - 10$ hours.

After the final impregnation, the semi-finished product is fixed on the mandrel and the thermal treatment lasts 2 – 4 hours at temperature 135 °C. The pressure is set equal to 0.2 MPa when processing a sidewall and 1 MPa when processing a front board. Taking into account the time of
temperature rise and its reduction to normal value, the duration of thermal treatment operation takes 18 hours.

The duration of impregnation is important for the organization of technological process. The duration of liquid impregnation of a solid medium with an open porosity is defined in accordance with the Darcy equation [25]:

$$q_p = \frac{K_D \Delta p}{\eta_C l}$$

(1)

where, $q_p$ is the liquid volume proceeding in unit of time through unit of area of section of porous material, $\eta_C$ is the viscosity of the liquid binder, $\Delta p$ is the pressure difference inside the solid medium filled with fluid, $l$ is the maximum path length through which the fluid passes when filling the pore space, and $K_D$ is the Darcy-Kozeny-Pocket factor [17].

Alcohol addition to the binder reduces the viscosity and the impregnation process duration $D_i$ (figure 4), but increases the residual porosity $P_0$ during drying. Initial data for calculation is selected so that the binder content in the TPC finished material would be at $28 - 30\%$, and the fibre content in the TPC finished material $67 - 70\%$. The workpiece size intended for impregnation is $l = 800 \text{ mm}$.

![Figure 4. Changes of porosity (a) and (b) binder impregnation process duration of the woven workpiece depending on impregnation number and the percentage of alcohol in the binder solution.](image-url)
As it is shown in experiments with resin B71731AL\[12, 13, 21, 23\], a reduction of binder viscosity can be expected by the introduction of carbon nanotubes (CNT).

3. The joint processes of binder curing and compacting of composite thermal protection filler in the autoclave

The processes of binder curing and compacting of the composite thermal protection filler are based on the possible uses of the RSCE autoclave.

The autoclave plant (figure 5) is a stand-alone automated system, integrating a thermally insulated vertical high pressure vessel, with a volume of 293 m\(^3\), the diameter of working space is 5.5 m, and the height is 6 m. The autoclave includes also: heating and cooling blocks, gaseous nitrogen compressed to 3.5 MPa production station, the nitrogen cumulative installation with the capacity of 300 m\(^3\), the vacuum station, the water conditioning unit with graduation towers and the chemical treating assembly of pipelines.

![Autoclave plant for DS composite structures forming](image)

**Figure 5.** Autoclave plant for DS composite structures forming:
1 – Nitrogen cumulative installation; 2 – Nitrogen plant; 3 – Vacuum station; 4 – Autoclave.

Special attention is paid to create conditions for a minimum temperature gradient on products during heating, thermostatic control and cooling, as well as to ensure even distribution of the binder in the material in case of multilayer, large-dimension and complex shape objects.

To achieve this result, the circulation system of coolant laminar flow movement with an optimum orientation relative to the product surface was developed (figure 6). On this plant basis, the thermal protection in neutral environment technology was developed for the transport spaceship “Soyuz TMA”. This technology provides reliability and stability of production, thermal protection quality and improved reliability, an increase of labor productivity and the reduction of expense of the electric power.
An autoclave control system enables change in pressure and temperature by pre-set programs $p(t)$ and $T(t)$. A control program must be selected to cure the binder and seal the filler structure with a minimum of compressed nitrogen. The program selection procedure is a complex scientific task, which mathematically requires detailed discussion.

The medium used in the autoclave is nitrogen which is obtained from air at the autoclave nitrogen plant and is pressurized by a compressor up to the receiver pressure. If required, nitrogen is supplied from the receiver to the reaction chamber, thus, creating the required pressure. The reaction chamber temperature is changed by nitrogen heating with varied power thermoelectric heaters.

There are five thermoelectric heater circuits in the autoclave, for each control stage of electric power. A fan located at the lower point of the reaction chamber provides heated nitrogen flow between the chamber walls. Near to the cover, on the top of the reaction chamber, the flow turns back to the centrally located product.

The law of product temperature variation with time and thermoelectric heater power during the autoclave treatment is selected on the base of practical experience of the product quality assurance. Thermoelectric heater power and temperature were recorded by a control system (figures 7 and 8) and used at determination of specific features of the autoclave.

![Diagram](image_url)

**Figure 6.** Scheme of nitrogen heating and movement in reaction chamber of autoclave with the following parameters:
1 — receiver;  
2 — reaction chamber;  
3 — DS thermal protection cover workpiece;  
4 — fan;  
5 — heater;  
6 — heat exchanger

![Graph](image_url)

**Figure 7.** Temperature $T$ variation during heat treatment of the product.
There are four sections in the temperature variation curve, where temperature variation rate $\dot{T}$ was selected equal to 10, 1.67 and 3.33 K/hour. In order to reduce the time required for heat treatment to eliminate significant deterioration of product quality on the 1st and 3rd sections, the temperature rate was increased compared to the recommended rate on the 2nd section.

The temperature variation rate is defined as follows, $\dot{T} = \frac{1}{\bar{t} \delta}$, where $\delta$ is the wall thickness of the product, $\bar{t} = \text{constant}$ is the recommended temperature rise by one degree assigned to the wall thickness unit. The proposed recommendations on the selection of thermoelectric heater power may relate to various structural elements of the thermal protection of descent spaceships.

The correlation of temperature-to-electric power based on the heat-transfer response rate can be described using the following equation

$$\frac{dT}{dt} + \mu T = \chi W$$

where $\mu$ is the factor of process response rate of the heat transferred from thermoelectric heat to the product.

The determination of the factors $\chi$ and $\mu$ is an important stage of establishing the procedure aimed to correlate autoclave nitrogen supply and temperature variation of composite products when the matrix is cured. Based on the data obtained by joint analysis using autoclave control instrumentation (the analysis was conducted on the four heating sections for stepwise thermoelectric heater circuit control), the following factor values were set as $\chi = 0.0972$ K kW\(^{-1}\) h\(^{-1}\) and $\mu = 0.0745$ h\(^{-1}\).

Nitrogen pressure is varied at the same time when the temperature of the product in the autoclave rises. It enables the combination of the process of binder curing and filler sealing in the product wall, from remains of the binder extruded from the work-piece.

The wall thickness variation law is obtained after the Darcy equation, (1) is re-arranged

$$\frac{d \ln \delta}{dx} = -\frac{2K^*_k \Delta T_m \Delta p}{R^2 + 2RH \frac{T}{\eta_0 \eta(x)}}$$

where $K^*_k = K_k R/(R + H)$ is a factor which considers the complex geometry of product side surface profile, $R$ and $H$ are the radius and height of the product, $\eta_0^*$ is the binder viscosity at the initial instant
at normal temperature, \( x = \Delta T / \Delta T_m \), and \( \Delta T_m \) is the maximum temperature differential during the autoclave treatment.

The dependence of dimensionless viscosity \( \eta \) on relative temperature \( x \) was obtained as an approximation result from experimental data. Thus, the data was obtained for epoxy-based binder ENFB/3692 [18, 22] which is approximated by the following formula

\[
\eta = \frac{b \exp(-\beta_T x)}{(1 - ax)^n}
\]

(4)

and as shown in figure 9, where the numerator means the viscosity drop when heated, and the denominator means the viscosity increase as a result of polymerization. \( a \), \( b \) and \( n \) are empirical factors that have to be defined using figure 4, where the constants are as follows: \( a = 0.997 \), \( b = 0.3 \), \( n = 1 \), and \( \beta_T = 4.8283 \).

![Figure 9. Nondimensional viscosity, \( \eta \), vs. relative temperature \( x \).](image)

![Figure 10. Time-line for the manufacturing process illustrated in nondimensional time.](image)
Figure 11. Nitrogen pressure differential amplitude, $\Delta p$, vs. nondimensional time, $\theta$, during the isobaric heating of the nitrogen. The quantity $t_k$ represents the relationship between the time taken to achieve the required binder volume fraction and the heating of the product.

Figure 12. The power cost to obtain the required nitrogen mass vs. nondimensional time, $\theta$, during the isobaric heating of the nitrogen. Continuous and dotted lines correspond to the economic and progressive modes, respectively, of the filling of the autoclave with nitrogen.

After the integration of equation (3), the correlation between the instant of nitrogen supply and its autoclave pressure differential amplitude appears, figure 11. The thermal effect on nitrogen-side thermal protection includes nitrogen refrigeration when it is adiabatically supplied from the receiver, nitrogen heating at first at the constant volume, and then with a constant pressure. The required variation of temperature is provided as a result.

For this purpose the automatic equipment of the autoclave carries out a step change of power of thermoelectric heaters and step supply of nitrogen, as represented in figure 8.
Figure 13. Comparison of theoretical and experimental recommendations on pressure $\Delta p$ in time $t$. The continuous line represents the practical recommendation, and the dashed lines are theoretical recommendations corresponding to different values of $t_{k1}$ and $t_{k2}$.

It is convenient to present the key processing events in terms of dimensionless time, $t$, which is obtained by dividing the actual time by the duration of the heating process, see figure 10.

The production cycle can be carried out in accordance with either the economic or progressive modes. The preparation stage for the operation of the autoclave, shown in negative area of dimensionless time, involves the filling of the autoclave reaction chamber with nitrogen. This stage of the economy mode consists of: creation of vacuum in the chamber; releasing nitrogen, of mass $m_0$ from the receiver and heating until the pressure reaches $p_0 = 10^5$ Pa at room temperature $20^\circ C$. The first stage of the progressive mode consists of pressurizing the nitrogen in the chamber before reaching the required concentration.

The second stage is identical in both modes. It includes isobaric heating of nitrogen at $p_0$ until dimensionless time, $\theta$. At this moment the additional mass of nitrogen, $\Delta m$, enters the chamber, and electric heaters maintain the temperature. This leads to an increased nitrogen pressure, $p_0 + \Delta p$, which influences the rate of displacement of excess binder volume from the workpiece. The displacement process at uniform heating and constant pressure and comes to the end at a time, $t_k \leq 1$ (≈ 1), when the required fibre-matrix volume fraction in composite material of thermal protection is reached.

In this paper, it is recommended to use variable-based power consumption as a selection criterion for instant of time

$$E^{v\alpha} = E_{00} + E_0 + \Delta E_1 + \Delta E_2 + E_1 + E_2$$

(5)

where $E_{00} = m_0 E_{N_2}$ is the power cost to obtain nitrogen mass $m_0$ from air and to compress it up to receiver pressure, $E_{N_2}$ is the power cost to supply 1 kg of nitrogen from nitrogen plant, fitted in the used autoclave to receiver, $E_0$ is the power consumption to restore temperature in nitrogen with mass $m_0$, $\Delta E_1$ is the power cost to obtain nitrogen with mass $\Delta m$ from air and to compress it up to receiver pressure, $\Delta E_2$ is the power consumption to restore the temperature in nitrogen with mass $\Delta m$, $E_1$ and $E_2$ are the power consumptions during an even increase of the product temperature before and after nitrogen auxiliary supplied to autoclave, accordingly.
When cost-saving and progressive pressure and temperature control algorithms are implemented, the calculation results of variable-based power consumption are represented in figure 12.

The nondimensional time values are defined in terms of actual times, as follows

\[ \theta = \frac{t_S}{t_T} \quad \text{and} \quad t_{ki} = \frac{t_R}{t_T} \]  

(6)

where \( t_S \) is the point in time when the additional mass of nitrogen was supplied, \( t_R \) is the time to achieve the required volume fraction, and \( t_T \) is the time at which the product heating stage was finished.

Analysis of the calculation result demonstrates that the power consumption at level \( \theta = 0.4 - 0.5 \) is minimum, therefore, the pressure variation shall be supplied after \( \theta > 0.5 - 0.6 \). Comparison of the proposed procedure and experimental application of the law of stepwise pressure variation is presented in figure 13.

The compatibility of instant of auxiliary nitrogen supply and nitrogen pressure variation amplitude is observed to be satisfactory. The mathematical models presented in the current work could be used for technological design of new spaceships.

4. Conclusions

A method is presented, demonstrating the effect of process duration and the number of repetitions on the impregnation operation, taking material porosity and binder viscosity into account. The method includes the calculation of the consumed mass of nitrogen, and for the consumption of electrical power for the receiving and heating of the nitrogen. It is shown that, to minimize the electrical power expense, there is a criterion for coordinating the moment of additional supply of nitrogen and the pressure amplitude. Comparison of the results obtained through calculation and experiment indicates that these techniques are highly effective.

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