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EXPERIMENTAL INVESTIGATION OF PYROCARBON FORMATIONS IN ABLATED LAYERS OF REINFORCED PLASTICS

V. V. Pasichnyi and V. N. Bulanov

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An experimental study has been made of the deposits of pyrocarbon in the process of ablation of two types of reinforced thermal-protection materials with a phenol-formaldehyde binder: glass-cloth laminate with an arrangement of the layers perpendicular to the direction of heating with a 25% content of carbon in the starting material and glass-cloth lavsan laminate with cloth layers parallel to heating (50% carbon). The experiments were conducted in a solar furnace with a ∅2.0 m concentrator for a constant heat flux of 50 W/cm^2 modeling the heating of the bottom part of rockets. Zones of active deposition of pyrocarbon have been established by layer-by-layer chemical analysis for carbon, based on which a structural scheme of the ablating layer of glass-cloth lavsan laminate has been proposed.

Reinforced plastics with organic and other binders are actively employed as ablating thermal-protective (heat-proof) materials for protection of spacecraft against aerodynamic heating upon entry into the dense layers of the atmosphere of the earth and other planets. During the "operation" of such thermal-protection materials, we have the ablation of them or thermal damage, which is accompanied by destruction, fusion, evaporation, high-temperature reactions, and other processes.

On the basis of theoretical prerequisities and experimental observations, Scala et al. [1, 2] have pointed to the possibility of formation of free carbon (pyrocarbon) deep in the ablating layer; this pyrocarbon can exert a certain influence on the thermophysical, thermomechanical, and other properties of the material destroyed. Pyrocarbon "heals" pores in the coke whose density and strength are improved but the gas permeability is reduced; the internal stresses and thermal diffusivity of this layer increase, which can have a negative effect on the protective properties of the coating. At the same time, works in which the process of deposition of pyrocarbon is investigated quantitatively in an actual ablating system are very few in number. Thus, in [3], a layer-to-layer chemical analysis of the carbonized part of a thermal-protection shield (made of phenolic glass-reinforced plastic) of a Mercury spacecraft has been made and the distribution of carbon, hydrogen, and oxygen over the thickness of the coked layer have been obtained; however, the zone of formation of pyrocarbon has been shown only for illustration without relation to the heat fluxes, the operating time, or the destruction rate.

In the present work, we have made an attempt to determine the conditions and qualitative pattern of formation of pyrocarbon in the ablating layer of materials operating for comparatively small heat fluxes and therefore having a small thickness in the actual version. In this case, the thickness of the destroyed layer can be comparable to the thickness of the coating, and any changes in the physical properties of the ablating layer can exert an appreciable influence on the entire thermal-protection material.

As the object of investigation, we have selected two model materials: 1) glass-cloth laminate with a phenol-formaldehyde binder with an initial carbon content of 25% and an arrangement of the layers in the cloth perpendicular to the specimen's axis and the direction of heating; 2) glass-cloth lavsan laminate with the same binder with a carbon content of about 50% and an arrangement of the cloth parallel to the direction of heating.

A solar furnace with a ∅2 m high-precision mirror concentrator, which allows an energy density of the order of 1 kW/cm^2 in a ∅10 mm focal spot, has been selected as the heating source. In our case the heat fluxes do not exceed 100 W/cm^2, which has allowed defocusing and an increase to ∅20 mm in the size of the specimens. The solar

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I. N. Frantsevich Institute of Problems of Materials Science, Kiev, Ukraine; email: pasich@ipms.kiev.ua. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 77, No. 3, pp. 16–18, May–June, 2004. Original article submitted March 27, 2003.

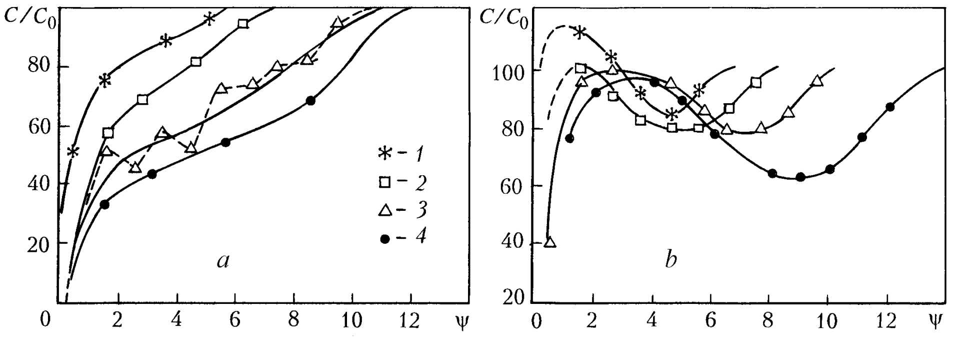

Fig. 1. Change in the relative content of carbon in the destroyed layer of material at different heating times: a) in glass-cloth laminate (1) 25, 2) 100, 3) 365, and 4) 625 sec); b) in glass-cloth lavsan laminate (1) 100, 2) 225, 3) 360, and 4) 400 sec.

furnace and the procedure of testing of the thermal-protection materials have been described in greater detail in [4]. There are two main reasons for the selection of the solar furnace instead of the traditional gasdynamic plants for heating of the specimens. First, the heating source — concentrated light — is very stable, sterile, and easy to measure and control, the heating can be carried out in an oxidizing air medium, etc. Second, the region of scheduled employment of the thermal-protection materials is the bottom part of the propulsion unit of the spacecraft, where the radiation of reactive gas jets is the predominant source of heating [5].

To determine the carbon content in the destroyed layer, the specimens tested for a constant heat flux of 50 W/cm^2 and at a variable time of heating with subsequent argon quenching were cut layer by layer every 1 mm with a special cutting tool for sampling.

The pattern of formation of pyrocarbon can be represented as follows. The thermodestruction of the binder and the organic fillers occurs in the deep-seated layers of material; the relatively high-molecular-weight compounds formed arrive at a hotter zone, where they are decomposed to form carbon and gases with a lower molecular weight down to hydrogen and carbon monoxide.

Based on the initial prerequisities, the ablating layer of glass-cloth lavsan laminate must form pyrocarbon more easily than that of glass-cloth laminate. This has been confirmed by the results of chemical analysis. As is seen from Fig. 1a, the content of carbon in the coked layer of glass-cloth laminate monotonically decreases with increase in the heating time and distance from the pyrolysis zone, which is explained by the constant completion of the reactions and removal of the gaseous products. The given dependences are averaged, since we took sections of the samples in the plane where the glass-cloth layers were arranged and the arrangement of the actual results was wave-like (the dashed curve is an example of a heating time of 365 sec).

As was to be expected, in analyzing glass-cloth lavsan laminate, we found a considerable nonuniformity of the change in the carbon content over the thickness of the coked layer (Fig. 1b). In the specimens whose heating time exceeded 50 sec and the thickness of the coke layer was no less than 3–4 mm, we observe an increase in the carbon content in the pyrolysis zone following its decrease; the increase is so intense that it can exceed the initial content. The carbon content sharply drops again as the heating surface is approached, due to the oxidation by the air oxygen and to the high-temperature reactions [3].

On the basis of the results obtained and for them to be explained, we have proposed a structural scheme (Fig. 2) of nonstationary ablation of glass lavsan, according to which we recognize four characteristic zones in the ablating layer:

(1) the pyrolysis zone, in which the basic low-temperature reactions of thermal decomposition occur, the gaseous products are released, the carbon content decreases, and the structure becomes porous;

(2) the zone of accumulation of pyrocarbon, in which we have dissociation of the gaseous hydrocarbons; the pyrocarbon formed fills the pores and makes the coke structure denser; the boundaries of this zone are determined by the minimum and maximum content of carbon;

(3) the zone of surface oxidation and high-temperature reactions, where the carbon content decreases and the coke structure is very porous and fragile;

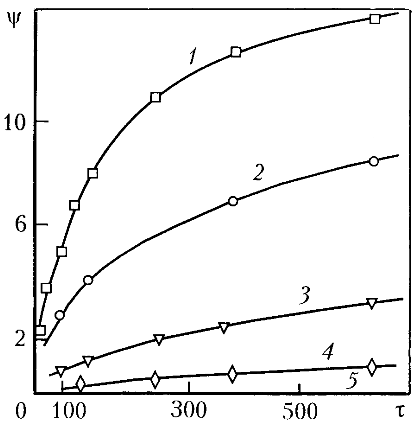

Fig. 2. Structural scheme of nonstationary ablation of glass-cloth lavsan laminate: 1) starting material; 2) destruction zone; 3) zone of accumulation of pyrocarbon; 4) surface-oxidation zone; 5) fusion zone.

(4) the zone of fusion of high-temperature reinforcing elements and fillers.

The recognition of these zones is very arbitrary, since their presence and dimensions depend on both the operating conditions and the characteristics of a material. Thus, in our case, when the heating times are short, the fourth and second zones are absent but, as the time increases, all the zones are extended, approaching constant dimensions if the material reaches the regime of quasistationary ablation. As the intensity of heating increases, the time of reaching the quasistationary regime is reduced and the ablation rate can become comparable to the rates of certain chemical reactions; therefore, the relation of the reaction zones changes.

The presence of the points of inflection on the curves (see Fig. 1b) demonstrates the reduction in the intensity of carbon loss in certain zones of the ablating layer. Therefore, we can state that the formation of pyrocarbon occurred in the case of glass-cloth laminate, too, but the intensity of the processes was much lower than that in glass-cloth lavsan laminate. The presence of lavsan fibers contributes to a more intense deposition of carbon not only due to the higher content of hydrocarbons in the material but also owing to the formation of directional channels for motion of gases in the coked layer as a result of their pyrolysis. Furthermore, the pyrolysis products of lavsan form pyrocarbon at lower temperatures than phenolic resins do.

NOTATION

C and C_0, carbon content in the running cross section of the destroyed layer and in the starting material respectively (C/C_0, %); ψ, depth of the destroyed layer, mm; τ, heating time, sec.

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