Thermal protection material on the base of silicon-carbide ceramics

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Abstract. The results of the thermal tests of silicon carbide ceramics, developed by the authors, intended for prospective use as the outer layer of the combined thermal protection of returnable orbiters and hypersonic aircraft are presented. Tests have shown that the developed silicon carbide ceramics is characterized by high operating temperature (about 2000 °C), resistance to thermal shock (heating rate ~ 65 K/s), and can withstand high thermal loads (~ 7 MW/m²) for a considerable time. Under comparable conditions, the proposed material exceeds by 1.5–2.5 times the WCu pseudo-alloy in terms of the ablation rate of the mass, while it is 5.5 times lighter. Due to the presence of free silicon in the material, the absorption of large heat fluxes can occur due to the melting and evaporation of silicon. This fact has received experimental confirmation. The problem of reducing the catalytic activity of ceramics due to the layer of silicon dioxide formed on its surface is discussed.

1. Introduction

The creation of thermal protection materials is important for the returnable orbiters, as well as for hypersonic aircraft. Currently, there are a number of materials used for these purposes: ablative heat-shielding coatings based on textile and asbestos laminate [1]; ablating heat-shielding coatings with a polymer matrix [2]; highly porous heat-shielding tiles made from microfibers of silicon oxide and aluminum oxide [3, 4]. The heat-shielding effect of such tiles is associated with low thermal conductivity of materials. The time of their effective work is limited by the properties of the material and is measured by several minutes. The upper temperature limit of their work does not exceed 1500 K [1,2]. In recent years, this problem has received new impetus due to the development of hypersonic aircraft, which also need thermal protection of the payload. In this case, the materials should be efficient even at temperatures of about 2000 K, withstand high alternating force loads, and also have chemical and erosion resistance at high temperatures [2,5]. The fundamental difference between the two problems mentioned and the corresponding materials is in the working time of the material. For launching spacecraft, the characteristic time of exposure to extreme heat loads is several minutes, and for modern hypersonic aircraft it is higher by an order of magnitude and can reach several tens of minutes. This difference also imposes new requirements for thermal insulation materials. For example, carbon material is not able to withstand high temperatures in an oxidizing atmosphere for a long time.

Another important engineering task is the creation of rocket engine nozzles capable of withstanding high thermal loads associated with burning fuels for a long time. Standard ablative materials have a
high rate of destruction, which leads to a change in the surface geometry, which is unacceptable for jet engine nozzles. In this case, it is necessary to use materials that work on the absorption of the phase transition energy [6]. Classic material of this type is tungsten-copper pseudo-alloy [7]. The refractory tungsten matrix (T_m = 3420 °C) provides mechanical strength and stability of the product geometry, and copper melting (T_m = 1083 °C) and evaporation (T_{boil} = 2590 °C) in the pore space of the composite structure allows to dissipate excess energy due to the heat of phase transitions.

For the reasons described above, recently silicon carbide ceramics has been considered a promising material for thermal protection of aircrafts [2, 8-18]. When studying the possibility of using such ceramics, as a rule, the question of its heat resistance under the conditions of extreme thermal loads is considered. Investigation of heat resistance under the conditions of extreme thermal loads for such ceramics are mainly carried out on plasma benches. It is important to note such a significant feature of this ceramics as its catalytic activity at high temperatures [18]. For silicon carbide ceramics it is described in [16,17]. In work [15] the samples of silicon carbide ceramics (disks 20 mm in diameter, 4–5 mm thick) was tested in nitrogen plasma jet. When the sample is heated to T_w ≈ 1700 K the temperature of the front surface abruptly increases up to T_w ≈ 2500 K. The authors explain the temperature jump by the formation of a thermal barrier film with a high catalytic activity on the sample. For considered work, an increase in the catalytic activity of the surface leads to an increase in the specific heat flux to the sample from 112 to 472 W/cm². The authors [15] note that the high catalytic activity of the material is a result of the loss of SiO_2 film. It is emphasized that a small amount of SiO_2 on the surface of the sample was formed due to the oxidation of SiC during the manufacture of samples. The effect of reducing the catalytic activity of heat-resistant films of the complex composition ZrO_2-HfO_2-Y_2O_3-HfB_2-SiC with a thickness of several hundred microns deposited on the surface of silicon carbide ceramics is studied in [15]. In [17], the behaviour of ultra-high-temperature ZrB_2-SiC ceramics is investigated during plasma tests. The work notes that under certain conditions (high heat flux, constant plasmatron power), a fast and spontaneous rise in the surface temperature of the sample is observed. The authors of [17] associate such a temperature jump with a change in surface chemistry: loss of the surface protective oxide film of silicon dioxide and an increase in heat flux to the surface of the sample, due to chemical reactions.

2. Experimental

2.1. Problem formulation

In this paper, we consider a slightly different type of SiC ceramics containing free silicon. In such a material, a portion of the heat flux can be absorbed by the heat of phase transitions due to melting and evaporation of silicon. The authors of this work developed a technology for producing high-quality silicon carbide ceramics [19,20]. The samples of silicon carbide ceramics for heat protection purpose usually are obtained by the self-sintering method. The material is heated to a temperature close to the silicon carbide melting point. In this case there is no free silicon in ceramics. A feature of our material is the use of the reaction sintering process with the addition of a silicon. After the process of reaction sintering material remains about 15–20 vol. % of free silicon densely filling the porous space of a silicon carbide matrix. Therefore, we checked the effectiveness of the application of this material as an element of the external layer of composite thermal protection. The use of only one given material as a thermal protection is limited by its high coefficient of thermal conductivity [19]. In contrast to most of the works on this topic, this work focuses not only on the heat resistance of a material, but also on its absorption of heat flux due to phase transitions of melting and evaporation of silicon [21], by analogy with tungsten-copper material. We also considered the possible lower catalytic activity associated with the formation on the material surface of a large amount of silicon dioxide due to its melting and oxidation. Note that in this case, the refractory SiC matrix (T_m = 2730 °C) provides mechanical strength and stability of the product geometry, and melting (T_m = 1415°C) and evaporation (T_{boil} = 2350 °C) of silicon is responsible for absorbing thermal energy. But only in this case, the density of the material is approximately 5.5 times less than that for a tungsten-copper pseudo-alloy.
2.2. Sample preparation and testing

For testing were prepared 2 samples of silicon carbide ceramics with a diameter of 50 mm and a thickness of 11 mm (Fig. 1). Ceramic precursor passed one stage of impregnation with phenol-formaldehyde resin and carbonization. After this, the reaction sintering of the sample performed at a temperature of 1650 °C. After the reaction sintering of a large billet (Fig. 1a), samples for testing were made from it by grinding. Samples had a ledge for more secure anchoring in the test assembly. Next, the samples were mounted in a graphite mandrel with a diameter of 98.5 mm. The flexible thermocouple was joined to the back side of the samples. The thermocouple data were recorded on a personal computer through the X8CP signal recorder. For additional thermal insulation of the back side of the graphite mandrel, carbon and mullite silica felt were used.

The temperature on the front side of the sample, which perceives heat load, was measured using a high-temperature pyrometer with spectral ratio function Dieltest-TC5S (800 - 3600 °C) with a recording frequency of 3 measurements per second.

![Figure 1. Preparation of samples of silicon carbide ceramics (a) and assembly of materials for testing on the plasmatron (b): 1 is silicon carbide test disk; 2 is graphite mandrel; 3 is carbon insulation felt (5 mm), 4 is thermal insulation felt (10 mm).](image)

| Sample # | Sample material | Diameter / thickness, mm | Density of material, g/cm³ |
|----------|-----------------|--------------------------|---------------------------|
| 1        | Si/SiC ceramics (HMTI) | 50/11 | 3.01 |
| 2        | Si/SiC ceramics (HMTI) | 50/11 | 3.01 |
| 3        | Graphite        | 50/13 | 1.8  |
| 4        | Pseudo-alloy W-Cu (76 vol.% W, 24 vol.% Cu) | 40/3 | 16.5 |

The heat load was created by a high-temperature subsonic air jet generated by an electric arc plasmatron. The power of the plasmatron in all these experiments was 361 kW, the heat flux to the cold wall, measured using an uncooled copper sensor, was 770 W/cm². The stagnation pressure was equal to 0.05 bar. Note that the applied heat load was 7 times higher than in [15].

In the experiments four samples were tested - 2 samples of silicon carbide ceramics (Fig. 1) and 2 samples from graphite and tungsten-copper pseudo alloy of similar geometry for comparison (Table 1).
3. Results and discussion

The results of temperature measurements are presented in Figure 2. The microstructure and morphology of the surface of individual samples after testing is shown in Figures 3-4. The test time for all samples was 30–32 seconds. Note that the first 3-5 seconds after switching on the plasmatron, a brighter arc burning occurred, which led to the output of the pyrometer readings to the maximum of the measurement range (3600 °C). For this reason, the measurement data for the front surface temperature at the initial stage of heating were not taken into account.

Figure 2. The results of temperature measurements during the testing of samples of materials on a plasma stand: the first index of the number is the sample number in accordance with the Table 1; the second index is the type of measurements: 1 is the temperature of the back side of the sample, thermocouple measurements; 2 is temperature of the front side of the sample, pyrometric measurements

For the described conditions, the heating rate on the back side of the samples of silicon carbide was ~ 65 K/s; for tungsten-copper pseudo-alloy ~ 140 K/s; for graphite ~ 55 K/s. The maximum temperature reached on the surface of tungsten-copper material was 2700 °C, graphite sample - 2100 °C. For the first material the discussed effect associated with the melting of the one component was quite clearly manifested. A sample of a tungsten-copper pseudo-alloy, after 8–10 seconds of heating, reached a stationary temperature regime caused by the melting and evaporation of copper (Fig. 2). Moreover, the temperature of the front surface of the sample correlated well with the evaporation temperature of copper, and the back side temperature with the melting temperature of copper. The linear ablation rate of the sample thickness under the test conditions was 20 μm/s, the mass destruction rate was 0.04 g/(cm² s).

The silicon carbide samples heated up slower (Fig. 2). After 13–17 seconds of heating, the front surface temperature stabilized at 1900 °C, and the internal surface temperature continued to
Figure 3. The sample of silicon carbide ceramics (# 2 in table 1) after testing (a), and the morphology of SiO₂ microparticles (b – f) formed on its surface (electron microscope images)

monotonously increase with a slight bend (deceleration) over a time interval of 15–20 seconds in the 1100 region °C. This kink is probably associated with the onset of intense silicon melting in the inner regions of the sample, since the average temperature of the sample in this time range was 1400-1500 °C. Further, both samples of silicon carbide ceramics behaved identically - approximately at the same time interval (17–27 sec. for the first sample, 13–23 sec. for the second one), the surface temperature rather quickly increased by 500 °C up to 2400 °C. Perhaps this was a manifestation of the effects discussed above and related to the catalytic activity of the material. Note that in [15], at a heat flux of about 110 W/cm², the surface temperature of similar ceramics increased from 2000 °C to 2800 °C, i.e.
by 800 °C. In our case, at a heat flux of 770 W/cm², the sample temperature increased from an initial level of 1900 °C, close to those one in paper [15], but only to 2400 °C. Direct comparison in this case is not entirely correct (different test times), but this feature and the observed difference of 400 °C may be crucial in practical applications.

All samples retained their mechanical integrity after testing (see, for example, Fig. 3a). Under the test conditions, the linear ablation rate of the SiC sample was 8 μm/s (2.5 times less than that of pseudo-alloy WCu), the mass destruction rate was 0.026 g/(cm² s), or 1.6 times less than that for WCu. For comparison, the linear ablation rate for a graphite sample under these conditions was 54 μm/s, and for fluoroplastic sample this rate is 440 - 490 μm/s.

Figure 4. The microstructure of the material in the cross section of a sample of silicon carbide ceramics (# 1 in Table 1) after the tests

The morphology of the sample surface after testing was investigated. On samples of silicon carbide ceramics in the process of testing, after about 20th second of thermal loading, yellow sparks dispersion was observed. We associate the formation of such sparks with the melting of silicon, its release on the surface in the form of droplets and their blown up by a plasma jet with simultaneous oxidation (burning) in an air atmosphere. This is indirectly confirmed by the following data. On the surface of silicon carbide samples, the formation of a continuous layer of white thin coating consisting of small spheroidal particles was observed (Fig. 3b, c, f). This layer material was collected for analysis. According to EDX analysis, all particles consisted only of silicon dioxide.

As mentioned above, according to the data of [16-18], the catalytic activity of the sample strongly correlates with the presence of silicon dioxide on the surface. The film of this material suppresses such activity. Perhaps the formation of a large amount of silicon dioxide on the surface of our material may be its advantage when used as a heat shield.
The morphology of the formed SiO$_2$ particles is presented in Figures 3b - 3f. The silica particles have a wide hierarchy of structures. They are presented as rather large droplets with a diameter of several hundred microns (Fig. 3b), and micron (Fig. 3f) and even submicron (Fig. 3c,e) particles. They were probably formed during crystallization from a melt of silicon. The variety of the obtained microstructures and their sizes testifies to the complex physicochemical processes that took place during their formation (evaporation, condensation, oxidation, etc.). Note that in these drops the processes of boiling and evaporation of silicon could also occur, as evidenced by numerous pores (Fig. 3d, e).

The internal structure of the material after testing was investigated. The results are presented in Fig. 4. The silicon carbide particles on these pictures have a darker color, the areas filled with silicon are lighter. Pores can be identified by black color. As can be seen, the pores formed from melting and removal of silicon (capillary uplift, evaporation) are observed at a depth of 1.5 mm from the surface of the sample (Fig. 4a). Note that the surface on which the heat flux fell corresponds to the upper part of Figure 4a. The silicon carbide matrix of the material consisted of two fractions - particles with characteristic sizes of 50 and 5 microns. Free silicon filled the pore space between the particles. The typical sizes of the silicon regions were from several microns to tens of microns. This correlates with the size of the observed pores. Inside the pores, a fine fraction of silicon carbide particles is observed (Fig. 4d).

4. Conclusion
The developed silicon carbide ceramics is characterized by a high operating temperature and resistance to thermal shock, and can withstand high thermal loads (~ 7 MW/m$^2$) for a considerable time. Due to the presence of free silicon in the material, the absorption of heat fluxes can occur due to the melting and evaporation of silicon. This fact has received experimental confirmation. Moreover, the formation of a significant amount of silicon dioxide on the surface of the material during its heating can serve as a factor in reducing the catalytic activity of the material. This allows decrease the thermal load on the aircraft during its flight in an air atmosphere. Possible directions for improving the heat-shielding characteristics of the material are associated with the modifications of the technological process, which allow an increase in the amount of free silicon in the silicon carbide matrix, as well as with the reinforcement of the material with special ceramic fibers.

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