EXPERIMENTAL STUDY OF SILICON CARBIDE OXIDATION AND CATALYTIC ACTIVITY IN DISSOCIATED FLOWS OF NITROGEN AND AIR

V.I. Vlasov, G.N. Zalogin, B.A. Zemliansky, V.B. Knotko
Central Research Institute of Machine-Building, Russia

Silicon carbide is a very promising thermal protection and constructional material, which is widely applied in rocket and space engineering. This material is used also as an anti-oxidizing coating for carbon-based materials. Just for such purpose this material was used for carbon front shield of OREX re-entry vehicle [1]. Earlier such kind of study was made for RPP coating on the carbon materials, which were applied for nose and wing edges of Space Shuttle orbiter [2]. Thermal and anti-oxidizing stability of SiC to the influence of oxygen atom at high temperatures were studied using high-temperature facilities of different types [3-5]. The main purpose of those investigations was the study of mass loss and surface property variation under action of oxygen atom.

It is found that SiC oxidation proceeds in two regimes – active and passive – depending on surface temperature T_w and external conditions (mainly on partial pressure of oxygen). In passive oxidation mode a SiO_2 film is generated on the surface of SiC, as result the mass of sample increases in some cases while testing in different facilities. In active oxidation the film is not generated on the surface, so the dissociated air interacts with original material.

The purpose of this work is an experimental study of processes concerning mass loss of silicon carbide and heterogeneous recombination of oxygen atoms on the surface of material at high temperatures, as well as finding the interrelationship of these processes.

The experiments were carried out in subsonic flow of air and nitrogen dissociated in high frequency plasmatron [6]. Research results of catalycity (γ, probability of recombination) are presented in [7] for this material at temperatures $1270 < T_w < 1700$ K (nitrogen) and $1290 < T_w < 1850$ K (air), pressure $p = 10$, 25, 30 and 50 *mbar,* stagnation enthalpy $H_0 = 19....33$ *MJ/kg*.

In order to determine the probabilities of atoms recombination on SiC surface the experimental heat exchange data were processed using special technique [8].

The temperature range was extended by varying the energy consumption and by using sample holders of 150 and 50 mm in diameter. Flow parameters were determined according to procedure [9] taking into account a possible deviation of flow state from equilibrium state. In these runs the temperature was measured with thermocouple, located in isothermal cavity behind the sample.

In the case the hot end of thermocouple does not touch the sample surface. The difference between measured temperature and surface temperature T_w, as well as heat losses (heat leakage) out from the sample were calculated according to [10] and were taken into account when processing the experimental data. The required heat flux distribution on the holder surface were determined using results of calculation the plasma flow around the holder in HF-plasmatron on the base of solution of Navier-Stokes equations [11].

In Fig.1 there are presented the dependencies of recombination probability,γ_N , and product of values $\gamma_N p_N$ on the SiC surface as function of 1/T determined in nitrogen flow. As for tile thermal protection of Buran orbiter, the value of γ_N for SiC depends on partial pressures of atoms, and the $\gamma_N p_N$ product in logarithmic scale fall practically on the same straight line. Dotted line in Fig.1b marks the

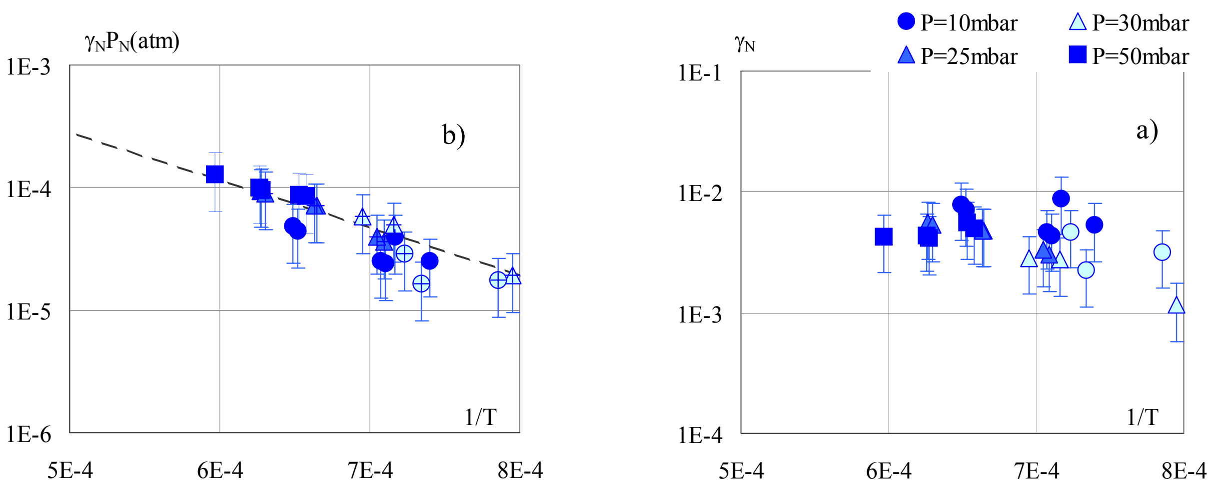

Fig. 1

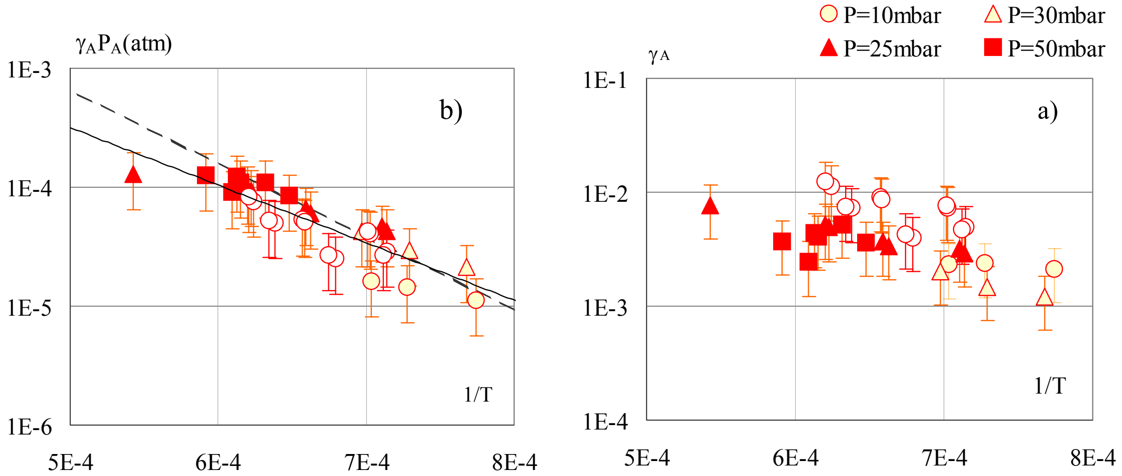

Fig. 2

data for tile thermal protection. As shown in the figure, the values are close one another in all temperature range. In Fig.2 there are presented effective values of γ_A and $\gamma_A p_A$ in dissociated air in dependence of $1/T$ (the same legends as for Fig.1).

The analysis gives ground for statement that recombination of nitrogen and oxygen atoms on the SiC surface in the temperature range ($1300 < T < 1900$K) proceeds according to Langmuir-Hinshelwood mechanism.

At the same time the rate of recombination reaction does not depend on the pressure and recombination probability is inversely proportional to the pressure (more exactly to the partial pressure of atoms). The similar values of recombination probability γ and its inverse dependence are presented also in [12].

As in [2], in described experiments it was not observed a reduction of γ, related with atom desorption from surface at high temperatures.

The data presented in Fig.1 and 2 are determined at sufficiently great duration of experiment ($t \sim 300 \div 360$ s), when the temperature, measured by thermocouple, stops changing, i.e. when a film on the surface is completely formed. The presence of the SiO2 film on the sample after run is well observed using microscope even at low magnification (~20-power).

The dependencies of γp product (see Fig.1b and 2b) on $1/T$ are approximated by expressions:

$$\gamma_N p_N = 0.26\cdot10^3\, exp(-12850/T)\ mbar \text{ and } \gamma_A p_A = 0.23\cdot10^3\, exp(-12800/T)\ mbar$$

The constants of rate for heterogeneous atom recombination on Langmuir-Hinshelwood mechanism, which were determined according to the procedure [8], look as

$$K = 1.1\cdot10^{-10}\, exp(-12850/T)\ m^2/s, \text{ (nitrogen)}$$
$$K = 0.94\cdot10^{-10}\, exp(-12800/T)\ m^2/s, \text{ (air)}$$

Maximum point (Fig. 3) is observed in tests with air flow, this maximum being absent in tests with nitrogen flow.

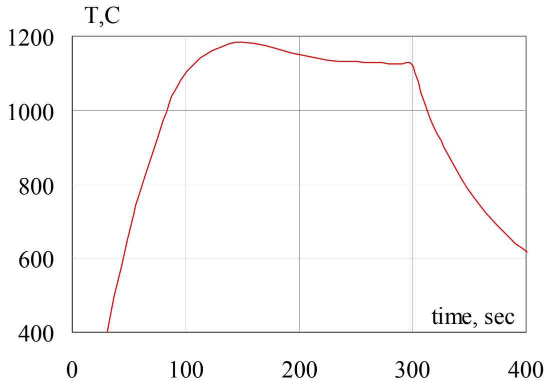

Fig. 3

One of possible explanation of this effect is modification of SiC surface catalycity due to growth of SiO_2 film under action of atom oxygen. These data testify to that probability values, γ (or catalycity K_w), experimentally determined in HF-plasmatron, could be used for flight conditions only taking into account their dependencies on the time in oxidative environment.

Analyzing curve in Fig.3 it is possible to conclude that the catalycity of pure material is higher than tested one, and this catalycity reduces under action of dissociated air on the sample, approaching to some constant value, close to the value for tiled thermal protection.

At the same time, according to the data in Fig.3, it is possible to evaluate the catalycity of the original material. For this purpose the data processing (prediction of γ) is carried out in some points starting from $T_{\max}$ to end temperature. In addition it is necessary to specify the temperature T^*, when film starts growing.

At short (in compare with the time of film forming) time of interaction between material and oxidative environment, at low temperatures ($T_w < 1000$K) or low partial pressures of atom oxygen there could be no appreciable change in catalycity on time (as in experiments [2]). In order to transfer predicted catalycity data to the conditions of real flight it is necessary to take into account the possibility of catalycity reduction in the course of SiO_2 film formation on the surface of original material.

Calculations of heat flux for *OREX* re-entry vehicle are performed according to the procedure [13]. The values of heterogeneous atom recombination probability on the SiC surface are determined based on the better coincidence of calculated and experimental data [1]. The results are presented in Fig.4. At high altitudes of flight (at low temperature T_w) the high probabilities γ_A of atom heterogeneous recombination are realized. As surface temperature increases during flight of re-entry vehicle along the trajectory the probability of recombination decreases (see diamonds in Fig.4) due to formation of SiO_2 film on the surface of the vehicle. In the region of maximal temperatures the values γ increases with temperature and are close to the results, predicted in HF-plasmatron.

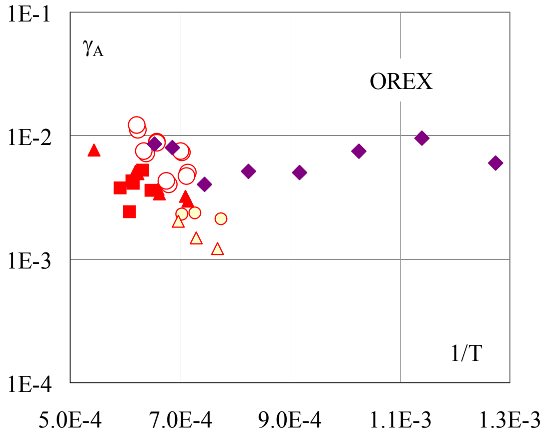

Fig. 4. ▲, ○, ■, Δ – HF-plasmatron

So the presented results testify to dependence of catalytic activity of silicon carbide not only on the temperature and partial pressures but on degree of coating the material surface by SiO_2 film. This degree itself is a function of time the dissociated air acting on the material. Experimental studies of thermal stability and SiC-based material catalycity should be carried out under conditions, reproducing not only pressure and surface temperature but also heat- and mass exchange coefficient [14].

Without taking into consideration the listed features of heat flux for *OREX* re-entry vehicle and possible modification of vehicle surface catalycity on degree of surface coating by SiO_2 film, it is hardly advisable finding more delicate effects such as formation of nitric oxide molecules [15] during heterogeneous reactions.

Flight conditions cause high difference between duration of oxygen atom action on thermal protection of re-entry vehicles of *OREX* type and gliding vehicles of Space Shuttle type. Thus it is necessary to take into account this fact when calculating surface heating for thermal protection based on SiC. In the first case the film on the surface is in the stage of formation due to short time ($\Delta t \leq 100$ s), in the second case ($\Delta t \sim 1000$ s) the dissociated air interacts with completely formed film during the flight along the most part of trajectory.

The study of mass loss for silicon carbide was performed in subsonic flow of TSNIIMASH's HF-plasmatron of 1 MW in power. The samples were made completely of SiC, or the carbon-based substrates were coated by CVD techniques. The experiments were carried out in dissociated air at three values of pressure $p = 10, 25$ and 50 mbar in temperature range $T_w = 1340 \dots 1660$K at stagnation enthalpy of $H_0 = 18 \dots 25$ MJ/kg. In air the pressure range was extended. A number of experiments was performed at pressures $p = 5.5, 75$ and 100 mbar. The temperature range equals $T_w = 1370 \dots 1870$ K at $H_0 = 16 \dots 35$ MJ/kg. Duration of plasma flow action to the sample at constant temperature equals 20 min.

In Fig.5 there is presented mass loss G per unit surface in nitrogen flow as function of $1/T$. The values of G, obtained at different pressures and depicted in logarithmic scale, fall well enough on the single straight line. Activation energies for reaction responsible for mass loss are also close one another.

The similar data for air are presented in Fig. 6. Unlike the nitrogen the values of mass loss in air are strong differentiate at various pressures and the slope of approximated curves (and hence, activation energy) is noticeable higher. The similar results in air were obtained earlier in [4]. These data are pre-

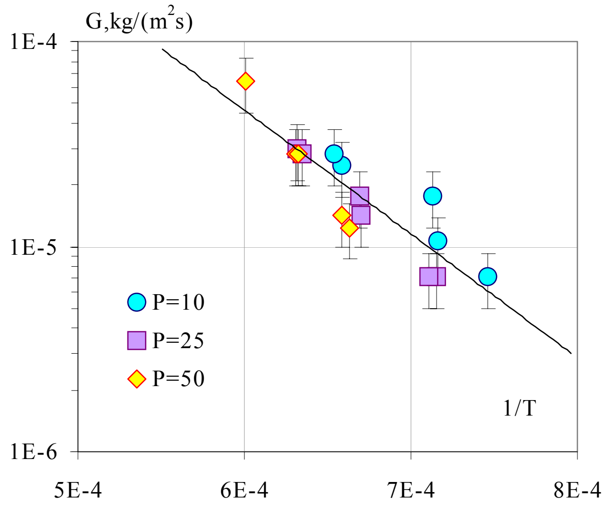

Fig. 5

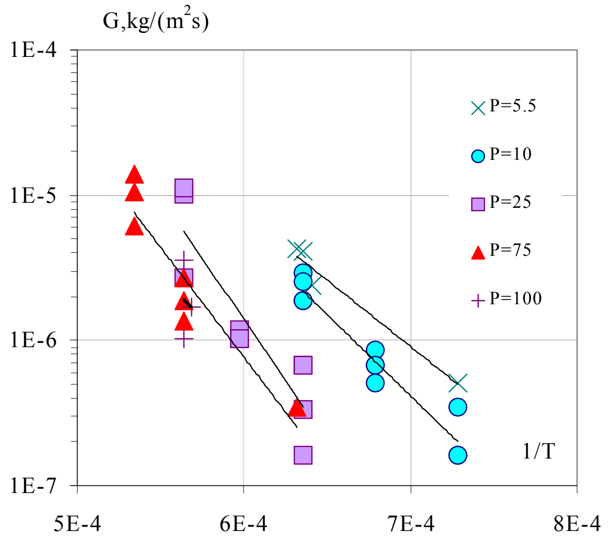

Fig. 6

sented in Fig.7. Experimental results for subsonic flows in HF-plasmatron match well enough as qualitatively so numerically. Experimental data are greatly dispersed because of small mass loss and possible adhesion of SiO_2 film to the holder during the runs.

The probability of mass loss process is noticeable lower (~ 100 times) than the probability of atom heterogeneous recombination. Thereof, thou more likely these processes are

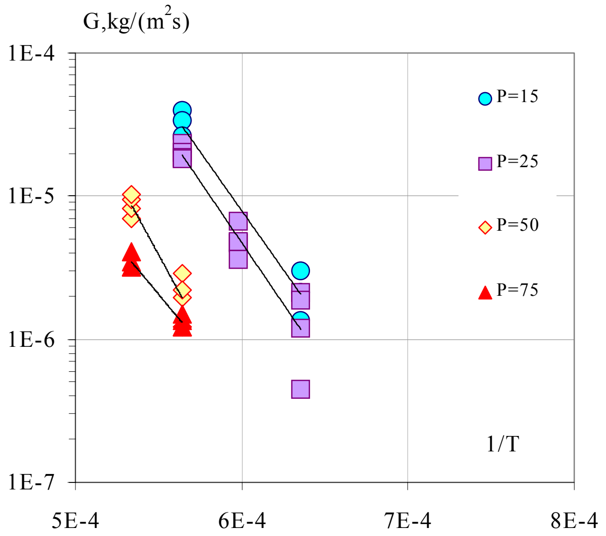

Fig. 7

interrelated, the mass loss at least in discussed range of conditions (T_w and p), cannot influence on the process of atom recombination and these effects could be considered separately. The distribution of material mass loss into energy balance is also negligible, and effect of pushing off ablation products due to blowing is also may be neglected.

Analysis of data, presented in Figs. 5 – 7, allows to make preliminary conclusions about mechanisms of mass loss for silicon carbide in dissociated air flow. The values of mass loss in flows of air and nitrogen are close one another at corresponding parameters. The similar results were obtained earlier in [2]. Relatively weak dependence of G value on pressure testifies that the probability of this process changes as $1/p$. That is in this case the process proceeds with participation of adsorbed atoms according to Langmuir-Hinshelwood mechanism and the rate of the process is governed by portion of surface, occupied by adsorbed atoms of nitrogen. In this case the most probable reaction is

1. $SiC + (N\text{–}S) \rightarrow \text{products} + S \qquad (1)$

Here S – active center of surface, (N–S) – chemically adsorbed atom of nitrogen. Rate of reaction (1) $R_1 = K_1\,\theta_N^2$. As shown the studies of SiC catalycity, in discussed temperature range T_w the surface is filled up with adsorbed atoms of nitrogen N. So it is possible to assume that $\theta_N \sim 1$. In this case the value $G \sim R_1$ does not depends on pressure, this fact corresponds to the experimental data. Catalytic sublimation [16] is another possible mechanism, which results in mass loss. In this case part of energy liberated at recombination of nitrogen atoms ($E = 9.8$ eV), goes into separation of SiC molecule from the surface. The similar values of activation energy for these processes, obtained in experiments ($E/k = 12850$ K and $E/k = 13880$ K for recombination and mass loss correspondingly), confirm the possibility of such mass loss mechanism. If this mechanism is realized, then the dependence of value G on pressure is also absent.

In dissociated air the dependence of the value G on pressure is close to $\sim 1/p$, and the probability of mass loss $\gamma_1 \sim 1/p^2$. In order to explain this fact let us consider the oxidation of SiC in oxygen atom environment In the temperature range with predominated Langmuir-Hinshelwood mechanism as mechanism of recombination, and when desorption of atoms from the surface is negligible, it should be considered 5 reactions:

2. $O + S \rightarrow (O–S)$
3. $(O–S) + (O–S) \rightarrow O_2 + S$
4. $SiC + (O–S) \rightarrow (Si–S) + CO$
5. $(Si–S) + (O–S) \rightarrow (SiO–S) + S$
6. $(SiO–S) \rightarrow SiO + S$

Here the symbols in the parenthesis means the adsorbed particles.

Taking into account that the probability of recombination $\gamma >> \gamma_1$, the part of free surface θ_s is determined from the first two equations. In steady state case

$$\theta_s = \frac{K_3}{K_2 n_O} \sim \frac{1}{p}$$

The mass loss is determined by reactions 4 and 6

$$G = K_4\, \theta_s \theta_O m_{CO} + K_6\, \theta_{SiO} m_{SiO}$$

In order to find the degree of surface filling by silicon and SiO we have equations

$$\frac{d\theta_{Si}}{dt} = K_4 \theta_s \theta_O - K_5 \theta_{Si} \theta_O$$
$$\frac{d\theta_{SiO}}{dt} = K_5 \theta_{Si} \theta_O - K_6 \theta_{SiO}$$

In steady state we obtain condition :

$$K_4\, \theta_s\theta_O = K_5\, \theta_{Si}\theta_O \text{ and } K_5\, \theta_{Si}\theta_O = K_6\, \theta_{SiO}$$

Taking these relation into account we have

$$G \sim (K_4 + K_5K_4/K_6)\, \theta_s \sim 1/p.$$

This result shows that relatively simple system for considered surface processes gives the proper dependence of mass loss on pressure. It is important that reaction which results in mass loss of SiC in nitrogen proceed on the part of surface occupied with adsorbed atoms, but in air these reaction proceed on the free surface. This fact explains the qualitative different dependence on pressure. It could be also assumed that their interference may appear through change of surface filling degree due to adsorption and reaction of recombination.

When analyzing SiC mass loss in dissociated air it is necessary take into account reaction (1) – (6). These systems should be completed with reactions of nitrogen atom adsorption and their recombination following Langmuir-Hinshelwood mechanism (similar to reaction 2 and 3) and reactions, which result in formation of SiO_2 molecules on the surface of material

$$(SiO–S) + (O–S) \rightarrow (SiO_2–S) + S \qquad (7)$$

It should be noted that reaction (7) determines only the rate of SiO_2 molecule formation. In order to determine the rate of film growth it is necessary to solve the corresponding differential equation.

The rate of SiO_2film growth can decrease due to reactions between these molecules and SiC. When surface temperature increases the role of desorption can increase. At this time the SiC mass loss in nitrogen flow decreases due to reduction of surface part occupied with atoms and sharply increases in air flow due to augmentation of free surface part.

All the existent and newly obtained experimental data and their analysis allow to conclude that in considered parameter range (T_w and p) the surface of SiC is partly covered with SiO_2 film, and this film can dramatically change catalytic activity of the surface and to a lesser degree influences on mass loss process.

Conclusions

1. The probability of atom heterogeneous recombination is experimentally predicted in dissociated flows of nitrogen and air on the surface of silicon carbide. It is found that process of atom recombination follows Langmuir-Hinshelwood mechanism and the constants of rate for these processes were determined in nitrogen and effective values of these constants in air.
2. It is shown that catalycity of silicon carbide may decreases under action of dissociated air due to growth of SiO_2 film.
3. The measured values of catalycity and features of its change under action of dissociated air are in well agreement with data of the flight experiment on the OREX re-entry vehicle.
4. On the base of analysis of experimental data on surface catalycity of material and mass loss during the experiment it was found the relation between these two processes. In particular it was shown that mass loss of SiC in nitrogen does not depend on pressure and this process proceeds on the part of the surface occupied with adsorbed atoms. At interaction with oxygen atoms the mass loss of SiC proceeds form the part of free surface which size is determined by the probability of atom heterogeneous recombination and decreases at pressure increases.
5. The proposed model of mass loss process adequately describes the dependence of mass loss on pressure.

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