SURFACE STRUCTURE DEGRADATION OF SI-BASED MATERIALS EXPOSED TO DISSOCIATED AIR AND NITROGEN FLOWS

O. Gerasimova[1], A. Kolesnikov[2], S. Borisov[1], A. Gordeev[2]

1 - Ural State University, Ekaterinburg, Russia
2 - Institute for Problems in Mechanics, Moscow, Russia

1. Introduction

Si-based structural materials (borosilicate, SiC, SiO_2) are widely used in gas dynamic systems that realize conditions of external and internal gas flow. The study of mechanism of gas interaction with a surface of these materials is a topical fundamental problem that has a wide spectrum of applications from the development of micro- and nano- scale gas driven devices (MEMS, microfluidics) to airspace. The complexity of the problem consists in the fact that the energy and momentum exchange between the gas and the surface depends on many factors, in particular, on nature and structure of the surface, gas pressure, degree of ionization/dissociation and other characteristics as well. The physical-chemical structure of the gas/surface interface controls the catalytic reactions on the surface with respect to O and N recombination and as a result defines the temperature conditions of space vehicles at the process of their re-entry into the planet atmosphere. Theoretical and experimental study of the energy and momentum transfer at the conditions that are similar to real ones allows to reveal characteristic laws and to construct adequate models of the surface processes.

New methods of scanning probe microscopy, in particular, atomic force microscopy (AFM) that is developed intensively last years give an opportunity to get information on specific features of the surface. This information must be taken into account to construct adequate boundary conditions for kinetic equations and describe correctly applied gas dynamics problems.

The main goal of this research is to investigate surface degradation process of Si-based samples as a result of long exposure to partially dissociated air and nitrogen flows at various surface and gas flow conditions. Scanning probe microscopy (AFM realization of Explorer Scanning Probe Microscope combined with Thermo Microscopes Proximal Probe Technology) is used for surface structure control. The samples of sintered SiC have been tested in subsonic high-enthalpy air and nitrogen flows using 100-kW IPG-4 plasmatron of Institute for Problems in Mechanics RAS, Moscow. They have been initially investigated by XPS technique with the goal of surface chemical composition attestation.

2. The SiC surface structure degradation in high-enthalpy air and nitrogen flows

Flat cylindrical samples for study have been prepared by cutting one SiC wafer. Every sample has 30 mm in diameter. Silicon carbide structure has been produced by sintering small grains (size < 5 microns) and has a density higher than 3.1 g/cm3. Two samples (SiC2 and SiC3) have been tested in subsonic high-enthalpy air and nitrogen flows of IPG-4 plasmatron under test conditions given in Table 1. The sample SiC1 presents the sample SiC2 before exposing to plasmatron.

Table 1. Test conditions

Sample number	Test regime	Test run duration, min	Working gas	Surface temperature, ^oC	Mass loss, mg
SiC2	N = 45kW, P = 78 hPa, G_{N2} = 2.4 g/s	8	Nitrogen	1555 => 1700*	11.25
SiC3	N = 29.5 kW, P = 78 hPa, G_{air} = 2.4 g/s	5	Air	1345	- 0.35

* - time dependence of the front surface temperature T_w is shown in Fig. 1

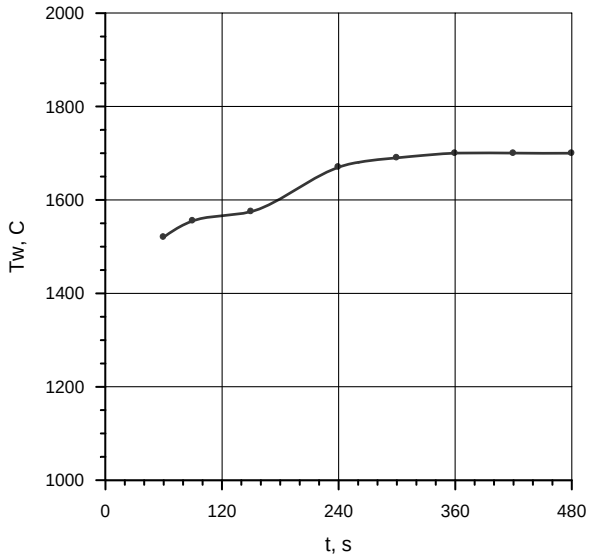


Figure 1. Time dependence of the front surface temperature T_w for SiC samples tested in dissociated nitrogen flow.

The X-ray Photoelectron Spectroscopy technique (XPS) has been used to analyze the chemical composition of the samples. The measurements were performed in an ultra high vacuum system with a base pressure of 10^{-8} Pa. The line of Mg Kα and Al Kα with the energy of 1253.6 eV and 1486 eV, correspondently, have been used as initial x-ray excitation. The surface is oxidized and covered with hydrocarbon contaminations. In order to study the chemical bonding of Si, C and O atoms the Si2p, Si2s and C1s core level spectra have been recorded. As it is possible to see from silica spectrum showed in Fig.2 the high-energy states from SiO_2 and basic states from SiC in 2p and 2s states are presented.

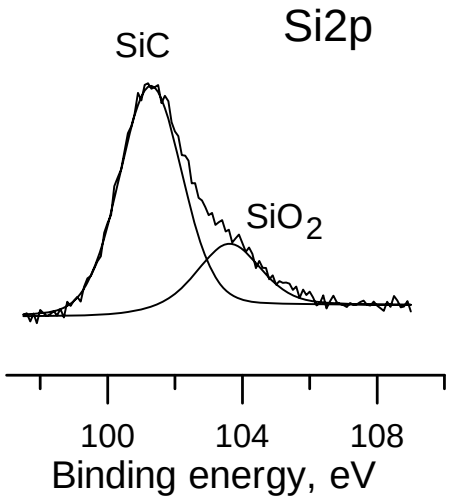


Figure 2. XP spectrum of Si2p-core layer of surface decomposed on the states from SiC and SiO_2

The atomic force microscopy measurements have been performed for characterization of the surface morphology evolution after exposing samples to gas flow. The area of scanning is varied from 100 μm to 1 μm depending on surface conditions (meaning the scale of the surface roughness). The scanning has been applied to different parts of the surface. Consequently, the different surface grains have been investigated. The images of typical SiC topography before and after exposure are shown in Figures 3.

The surface roughnesses parameters have been estimated using the topography images, in particular, root-mean square roughness, average height of microelements and fractal dimension. The results are presented in Table 2.

The roughness of the surface is defined by the root-mean square (RMS) roughness or fluctuation in the height [1] as:

$$\sigma = \frac{1}{N}\sqrt{\sum_{i}^{N}\left(h_i - < h_i >\right)^2} ,$$

where h_i is the measured surface height at point *i*; $< h_i >$ is the local value of the fitting plane. The summation is taken with respect to all points of every single matrix of data. The global surface roughness is obtained by averaging σ over a number of different topographies.

The mean height of the surface heterogeneity is given by the average height within the selected height profile. The mean height is calculated according to the standard definition:

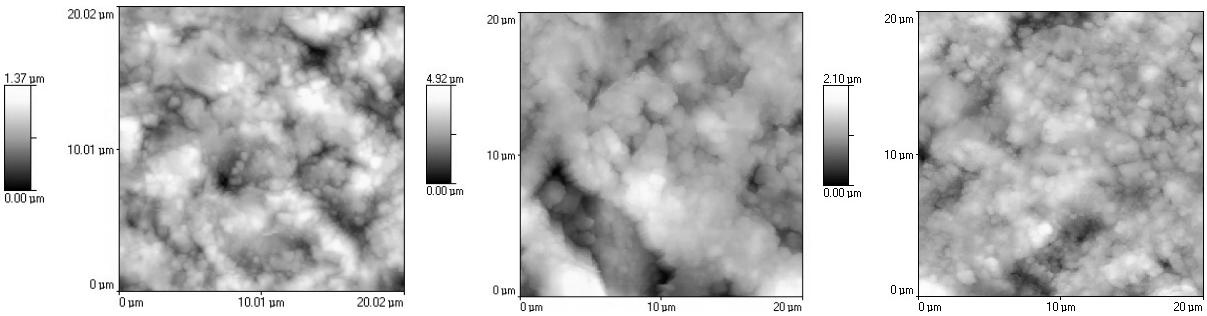
$$R_{ave} = \frac{1}{N}\sum_{i}^{N} h_i \ ,$$

where *N* is the number of data points within the height profile.

Fractal analysis has been performed in order to determine the spatial complexity of roughness. In fractal geometry a fractal dimension D_F is a non-integer parameter that is unique descriptor of an object, analogous to the integer dimensions in Euclidean geometry. There are a few algorithms that can be used to determine the fractal dimension of profiles. In this paper a two-dimensional variation method [2] is used to examine the fractal nature and estimate the fractal dimension of the surface.

Table 2. Parameters of the surface microstructure for three different samples

Sample	σ, nm	R_{ave}, nm	Peak spacing, μm	Peak angle, ^{o}	D_F
SiC1	272.4	1058.8	0.62	8.42	2.36
SiC2	673.1	2488.8	0.46	19.01	2.36
SiC3	236.3	1121.6	0.43	12.69	2.48



a) b) c)

Figure 3. Typical AFM images of (a) the sample before exposing, (b) the sample exposed to nitrogen and (c) the sample exposed to air.

3. Results

According to [3,4] the interaction between dissociated air flow (O_2, N_2, NO, N, O) and the catalytic surface can be described by the following catalytic reactions:

1) Adsorption and desorption of atoms

O+(S)⇆(O-S), N+(S)⇆(N-S)

2) Recombination between gas atoms and atoms adsorbed on the surface (ad-atoms) (Eley – Rideal recombination)

O+(O-S)⇆O_2+(S), N+(N-S)⇆N_2+(S),

O+(N-S)⇆NO+(S), N+(O-S)⇆NO+(S),

3) Recombination between ad-atoms (Langmuir – Hinshelwood recombination)

2(O-S)⇆O_2+2(S), 2(N-S)⇆N_2+2(S)

$(O\text{-}S)_m$+(N-S)⇆NO+2(S), $(N\text{-}S)_m$+(O-S)⇆NO+2(S)

4) Adsorption – desorption of molecules

O_2+(S)⇆(O_2-S), N_2+(S)⇆(N_2-S).

In the case of ionized or dissociated air flow (O_2, N_2, NO, NO^+, O_2^+, N_2^+, O, N) the reactions of dissociation-recombination; associative ionization and exchange reactions must be taken into account.

3.1. Oxidation effect

Chemical reactions of SiC with oxygen lead to the formation of SiO, SiO_2, CO and CO_2. Silicon carbide has two types of oxidation behavior, i.e. passive oxidation and active oxidation, depending on oxygen pressure at high temperatures [5-8]. The passive oxidation may be characterized by the formation of a protective SiO_2 layer accompanying mass gain:

$$SiC(s)+\frac{3}{2}O_2(g)\rightarrow SiO_2(s)+CO(g).$$

Here (s) and (g) correspond to solid phase and gas phase, respectively.

This oxide acts as a diffusion barrier during oxygen flux impacting at the surface. CO(g) formed at this interface escapes rapidly through the silica film. The formation of this stable SiO_2 film is called «passive oxidation». This process leads to weight gains of the sample.

At higher temperatures (above ~1400^0C) and lower oxygen pressures, a SiO_2-layer is removed and no stable SiO formation becomes more likely. This process is called «active oxidation» with weight losses.

As it is seen from the Table 1, small mass gain (0,35 mg) is observed after test run in dissociated airflow. It indicates on possible passive oxidation of SiC sample surface with formation of SiO_2 film.

The study of the oxidation is expected to yield important information on the critical processes that are determined by the morphology and microscopic defects in the film. When the SiO_2 layer grows, oxygen must penetrate through the oxide to the oxidizing interface. The uniformity of the interface is, thus, dependent on the uniformity of the oxygen supply to the moving SiO_2/SiC boundary. The latter depends on the smoothness of the surface and on the uniformity of the oxide formed so far. Since the oxide growth is non-uniform, the surface is likely to be much rougher after the removal of the oxide film. Thus, the surface of the samples after exposing to airflow that contains dissociated molecules becomes smoother than before exposition. Consequently, the root-mean square roughness σ becomes lower comparing to one for the sample before exposure: before experiment σ=272.4 nm and after exposing to airflow σ=236.3 nm.

3.2. Nitridation effect

To clean the surface of SiC sample dissociated nitrogen gas flow has been used. Effect of atomic nitrogen exposure on mass loss for SiC sample has been studied experimentally in [9] were mass loss rate has been found significant. Besides, mass loss observed in [10] for SiO_2 exposed to nitrogen flow was significantly higher than in airflow. Organic contamination was carbonized at high surface temperature and carbon is removed from the surface due to chemical interaction with atomic nitrogen [11]. Thus dissociated nitrogen allows removing from the surface silica film and organic contamination together with upper layer of SiC.

According to the model proposed by Jamet Ph. *et al* [12], nitridation effect involves two sets of mechanisms at the SiO_2–SiC interface: (1) creation of strong Si≡N bonds that passivate interface traps due to dangling and strained bonds and (2) removal of carbon and associated complex silicon–oxycarbon bonds. The mechanisms leading to creation of strong Si≡N bonds are completely analogous to the case of the SiO_2–Si interface [13]. In the case of both SiO_2–Si and SiO_2–SiC interfaces, there are Si bonds passivated by N, and strained Si–O bonds that are replaced by strong Si≡N bonds during the nitridation.

At the nitridation process the carbon removes from the interface. Most of the carbon atoms released by oxidation of the SiC substrate react with the existing oxygen to create CO molecules that diffuse out of the oxide. However, some of the released carbon atoms accumulate into carbon clusters acting as interface traps themselves and causing to the appearance of complex silicon oxycarbon compounds at the interface.

The topography data for samples exposed to nitrogen flow show that the surface roughness increases significantly compare to one for sample before exposing. The process of silica and carbon removal from the surface can be considered as one of the reason of such effect.

Significant increase in surface temperature from 1520 to 1700 ^{0}C (Figure 1) at constant parameters of dissociated nitrogen flow indicates increase in surface catalycity since surface emissivity of sintered SiC does not show significant changes during oxidation tests in the IPG-4 plasmatron [14]. Increase in surface catalytic activity could be caused by evaporation of low-catalytic film of SiO_2 and uncovered pure SiC, which demonstrates moderate catalycity in dissociated nitrogen [15]. Surface temperature attainment near the end of experiment confirms completion of stabilization and changes in the surface state.

4. Conclusions

The process of Si-based samples exposure to gas flow at various conditions that include time of exposure, surface temperature, gas nature can lead to significant change in surface chemical composition and microstructure. The AFM analysis shows that nitrogen gas flow interacting the SiC sample produces surface roughness that is higher than in the case of airflow exposure. This result can be explained not only by the change in gas composition but strong influence of surface temperature, time of exposure and as a result of mass loss. Parameters of the surface obtained with the use of AFM can be helpful for simulation of gas/surface interaction and estimation of surface roughness influence on energy and momentum exchange in internal and external gas flow problems.

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