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Determination of active nitridation reaction efficiency of graphite in inductively coupled plasma flows

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ABSTRACT

Accurate prediction of the gas-surface interaction during spacecraft reentry remains a challenging problem for thermal protection system design. Attempts to model the surface chemistry of ablating materials focus on oxidation and sublimation of the carbon surface, but usually neglect nitridation processes. Although nitridation may only lead to a minor increase in overall mass loss through ablation, it can highly impact other surface chemical processes through consumption of available atomic nitrogen, affecting the energy balance. We present experiments on graphite ablation in nitrogen plasmas, aiming at the determination of carbon nitridation reaction efficiencies in a relevant reentry environment reproduced in an inductively coupled plasma facility. The actual carbon nitridation reaction efficiencies are extracted using a numerical model with ablative boundary condition coupled to the flowfield. Emission spectroscopy of the CN radiation provides local CN species densities used for validation of the numerical model. The data are in-line with values reported in literature and extend the investigated temperature range. Our computed CN species densities agree well with the experimental values, providing confidence in our method. Based on our findings and additional literature data, we propose an updated Arrhenius form for evaluation of nitridation reaction efficiencies as a function of the wall temperature.

1. Introduction

Future space exploration missions aim at returning samples from Mars and asteroids to Earth for detailed chemistry and mineralogy analysis, as well as continuing the manned space exploration program. The aerodynamic drag during atmospheric entry for such missions transform the spacecraft's high kinetic energy into thermal energy through a strong shock wave in front of the vehicle. In the shock layer, gas temperatures may exceed 10,000 K and spacecraft are therefore equipped with a Thermal Protection System (TPS), shielding the crew and payload from the severe heating. Two main types of TPS exist. Reusable heat shields, generally carbon/silicon carbides (C/SiC), are passively cooled by reradiating most of the incoming energy back into the atmosphere. They can survive multiple mild atmospheric entries without major changes of mass and material properties. Ablative heat shields, in contrast, transform the thermal energy into decomposition and removal of the material. They are generally composed of a rigid composite, reinforced with a matrix of organic resins to serve as a pyrolyzing binder, producing a char that deposits on the surface followed by its ablation [1,2]. Removal of the carbon char is governed by surface reactions such as oxidation, nitridation, and sublimation. Selection and sizing of the Thermal Protection Material (TPM) are two key performance parameters in TPS design. Inaccurate prediction of the material response and its interaction with the flow field can be fatal for the crew or the success of robotic missions.

The current state of the art still lacks detailed experimental data on the gas-surface interaction occurring on carbon-based heat shields. This results in high safety factors for TPS design [3], caused by the lack of knowledge on dominant physico-chemical processes. With the numerical-experimental approach presented in this work, we want to contribute to the ongoing efforts of developing new thermochemical ablation models by providing accurate reaction efficiency for active nitridation of graphite.

Many experiments in the past were dedicated to the effects of oxygen as a main driver for carbon heat shield recession [4–9]. The

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nitridation reaction

$$C_s + N \rightarrow CN + 0.34\ eV \quad (1)$$

on a solid (s) carbon surface, which has been found to increase rapidly when the surface temperature exceeds 1400 K [10,11], is still weakly understood. For example, we have shown in a previous publication the impact of nitridation on a Carbon-Bonded Carbon Fiber (CBCF) preform material, which exhibited strong erosion of the carbon fibers at microscale after nitrogen ablation [12]. Nitridation reaction efficiencies proposed by Park and Bogdanoff [13] and Suzuki et al. [14] differ by several orders of magnitude. It is thus not surprising that numerical simulations of carbon-phenolic ablation using the Park and Bogdanoff nitridation data predicted higher mass blowing rates compared to calculations without nitridation [15]. However, due to the low exothermicity of the nitridation reaction (Eq. (1)) it does not directly have a significant influence on the wall heating rate. But no surface recombination reactions of any species were included in the model used. The wall heat flux, however, may be driven by recombination of available atomic nitrogen at the surface, and consequently, affected by the nitridation reaction efficiency. Even if nitridation does not cause much material ablation, it may significantly alter the N-atom recombination probability at the surface, hence the surface heating rate. This becomes especially important for carbon/silicon carbide composites (C/SiC), employed as reusable TPM, which ideally exhibit a low catalytic, highly emissive, and highly oxidation resistant surface. Studies beyond active oxidation of C/SiC materials in air plasmas suggested that nitrogen reactants actively participate to the chemistry of the surface. Particularly N-atom recombination may lead to a strong surface temperature increase [16–19]. Those findings were supported by additional experiments of identical C/SiC materials in pure nitrogen plasmas [20]. Beside the physico-chemical influence of nitridation on the surface heat flux, production of gaseous CN significantly contributes to the overall radiative heat flux for fast reentry vehicles [21,22] and non-equilibrium phenomena related to the electronically excited B state can cause additional radiative heating.

Because of the prohibitive high costs of real flight experiments, development and validation of surface chemistry models and coupled flow-material approaches rely on intensive ground testing in plasma wind tunnels. Although present wind-tunnel technology does not allow for a complete simulation of the hypersonic flight flow conditions in a ground facility, specific phenomena can be studied separately in a narrowed environment, where dominant parameters, such as heat flux, pressure and the resulting boundary layer chemistry, are close to the reentry environment [23,24]. The 1.2 MW Plasmatron facility at the von Karman Institute for Fluid Dynamics (VKI) is extensively used for the simulation of the aero-thermodynamic environment of reentry plasma flows in the boundary layer of a test object for a wide range of pressures and heat fluxes, creating a high-enthalpy, highly dissociated subsonic gas flow [25]. The gas is heated by induction through a coil, creating a high-purity plasma flow thanks to the absence of electrodes and their associated erosion. This particular characteristic makes the ICP plasma generators a perfect facility for the study of the complex gas-surface interaction, such as ablation and catalysis.

Simultaneously to the advances in plasma ground testing, multiple numerical tools have been developed at the VKI for simulation of reentry related phenomena. Within this work, we used jointly a stagnation-line code for reproduction of the flow field along the stagnation-line of a spherical body [26], and a surface ablation submodel developed to simulate the behavior of carbon-based ablative materials [27].

The two main objectives of the present work are the following:

a) Experimental-numerical determination of carbon nitridation at temperatures exceeding 2300 K (higher than those currently reported in the literature) based on an ablation model accounting for the carbon injection coupled to the boundary layer flow.
b) Validation of the numerical model through comparison of computed and spectroscopically measured CN species densities.

The main sections of the article cover the description of experimental methods (Sec. 2: the VKI Plasmatron facility, spectroscopic setup and data treatment to obtain local CN emission intensities, determination of CN species densities from spectroscopic data), description of numerical methods (Sec. 3: plasma flow rebuilding, stagnation-line model with ablative boundary condition), and experimental/numerical results and discussion (Sec. 4).

2. Experimental facility, measurement techniques and methods

The experimental setup installed at the Plasmatron facility offers intrusive and non-intrusive (optical) measurement techniques. The instrumentation equipment for this work consisted of a video camera, a 2-color pyrometer, a broad-band radiometer, a digital camera, and a spectrometer with intensified Charge-Coupled Device (CCD) (reviewed below). The main data of interest during this investigation were surface ablation rates of graphite in a pure nitrogen plasma, including measurements of the locally resolved CN boundary layer emission.

2.1. Plasmatron facility description

The Plasmatron is equipped with a 160 mm diameter Inductively Coupled Plasma (ICP) torch powered by a high-frequency, high-power, high-voltage (400 kHz, 1.2 MW, 2 kV) generator. The gas is heated by induction through a coil, providing a high-purity plasma flow. A hemispherical 25 mm radius copper water-cooled probe, mounting a copper calorimeter in the center of the front face, is used for heat flux measurements. The cold wall ($T_w \approx 350$ K) stagnation point heat flux is determined by the cooling water mass flow, controlled by a calibrated rotameter, and the inlet/outlet temperature difference, measured by two type-E thermocouples. A Teflon® insulator is inserted between the calorimeter and the probe's wall in order to have side-wall adiabatic conditions. Both the probe and calorimeter have copper surfaces which are highly catalytic to nitrogen and oxygen atoms recombination. The heat flux can be measured with ±10% accuracy. A water-cooled Pitot probe is used to perform stagnation pressure measurements. The pressure line is connected to a Validyne variable reluctance pressure transducer and a voltage demodulator amplifies the output. Validyne and amplifier are calibrated prior to the test by means of a Betz water manometer, leading to an uncertainty of ±0.2%. The Plasmatron chamber is also equipped with an absolute pressure transducer that measures the static pressure with ±2 Pa accuracy. The probes are mounted inside the Plasmatron test chamber at 0.445 m distance from the ICP torch exit. The placement ensures that the axis of the probe and the axis of the torch itself coincide.

2.2. Experimental setup and methods

The graphite test sample shape was a 25 mm radius hemisphere with a 25 mm long cylindric afterbody, machined in-house (a photograph can be found in Fig. 2). The raw graphite material was a superfine grain, high-density extruded graphite rod obtained from Graphtek LLC. We note that isomolded graphite might be another possibility for plasma tests due to its uniform properties, of great