Numerical Determination of Reaction Coefficient of Nitrogen Atoms with Solid Carbon by Using DSMC Method

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Abstract. We performed DSMC simulations of the supersonic nitrogen atomic flow measured in Park and Bogdanoff's experiment [*AIAA Paper*, 2003-158 (2003)] in order to determine reaction coefficient of nitrogen atoms with solid carbon. As a result of our numerical simulation, it is found that the reaction coefficient obtained in their experiment was overestimated by about 40%.

INTRODUCTION

Quite recently, spacecrafts started to bring samples back from a planet, an asteroid, and a comet by use of sample return capsules (SRC) entering Earth's atmosphere at a super-escape velocity, *e. g.*, Stardust of NASA [1,2] and Hayabusa of JAXA [3]. The SRCs are covered by carbonaceous heatshields, which can absorb high heating rates by ablating. The mass of the SRC must be minimized because the launch cost increases exponentially as the mass increases. Therefore, understanding of heating process of the ablating surface is important. Carbonaceous heatshields are made by impregnating a graphitic matrix with a hydrocarbon resin. During the entry flight, the resin pyrolyzes and the resulting gas escapes from the surface. The ablating surface becomes nearly pure carbon. The shock layer formed during the entry flight around the SRC will be totally dissociated [4]. Oxygen and nitrogen atoms can reach the carbon surface. It is well known that the atomic oxygen reacts with solid carbon to form carbon monoxide (CO) through the oxidation process

$$\mathrm{O} + \mathrm{C(c)} \rightarrow \mathrm{CO} + 3.74\,\mathrm{eV}, \tag{1}$$

where (c) signifies a crystalline state. The coefficient of this reaction has been measured in atomic beam experiments. It was found that the coefficient depends only on the wall temperature and varies from about 0.01 at room temperature to about 0.3 at 3000 K [5]. This process increases the rates of ablation and the heating. As shown in Fig. 1, atomic nitrogen may also undergo a process similar to Eq. (1):

$$\mathrm{N} + \mathrm{C(c)} \rightarrow \mathrm{CN} + 0.35\,\mathrm{eV}. \tag{2}$$

For the sake of expediency, this process is termed nitridation process here. The gaseous cyanogen molecules, CN, are likely to rapidly undergo the exchange reaction in the gas phase:

$$\mathrm{N} + \mathrm{CN} \rightarrow \mathrm{N_2} + \mathrm{C} + 2.04\,\mathrm{eV}. \tag{3}$$

Therefore, the net heat generated by the nitridation process is nearly equal to that of the oxidation process (1). Carbon atoms produced in the process (3) may condense on the ablating wall:

$$\mathrm{C} \rightarrow \mathrm{C(c)} + 7.4\,\mathrm{eV}. \tag{4}$$

A series of reactions after the nitridation process (2) is equivalent to the surface catalytic recombination of nitrogen atoms:

$$N + N + C(c) \rightarrow N_2 + C(c) + 9.8\,eV. \tag{5}$$

Nitrogen atoms will also impact on the solid carbon particles introduced into the boundary layer flow over an ablating heatshield.

Although the nitridation process (2) is expected to increase the heating as well as the oxidation process (1), the coefficient of the nitridation had not been investigated until recently. Park and Bogdanoff [4] measured this coefficient in a shock tube. Their experimental set up is shown schematically in Fig. 2. The driver was filled with helium to a pressure of about 6.8 atm. The driven section was filled with high purity nitrogen to a pressure of either 0.083 or 0.25 Torr. A grid of tungsten wire coated with carbon was placed in the test section which is 5.34 m downstream of the diaphragm. The grid consisted of 22 tungsten wires 0.0508 mm in diameter, spaced at 2.39 mm intervals, as indicated schematically in Fig. 3. Spectral intensity measurement was made across the flow through the lines of sight located about 9.7 mm downstream of the wire grid. As the dissociated test flow passes through the grid, nitrogen atoms strike the wires. If the surface reaction process (2) occurs, there will be CN molecules in the wake of the wires as shown schematically in Fig. 3. The concentration of CN was determined from the output from monochromator. In their work, the number of collisions between the nitrogen atoms and the wires was determined assuming a molecular beam without intermolecular collisions and the reaction probability of the nitridation was deduced by using the formula

$$\text{Reaction probability} = \frac{\text{CN concentration}}{\text{N concentration}} \div \frac{0.0508}{2.39}, \tag{6}$$

where the value 0.0508/2.39 signifies the fractional blockage of the flow by the wires. However, the mean free path of nitrogen atoms is smaller than the wire diameter, and hence the assumption of the molecular beam without intermolecular collisions is not valid. We simulate nitrogen atomic flow around the carbon wire measured in the experiment of Park and Bogdanoff [4] by using the direct simulation Monte Carlo (DSMC) method and determine the reaction probability of the nitridation process numerically.

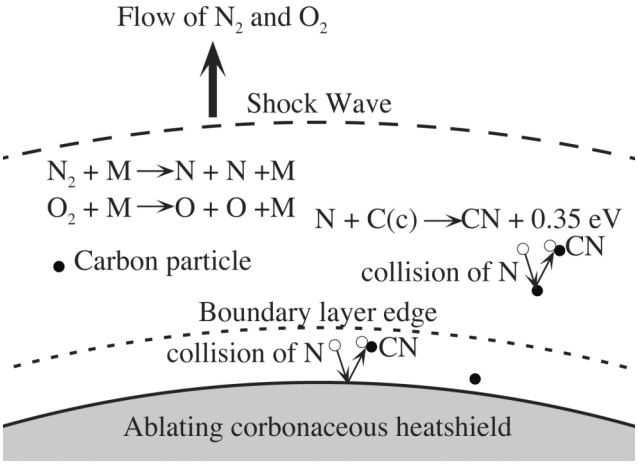

FIGURE 1. Schematic of the nitridation phenomenon in the shock layer flow over an ablating heatshield.

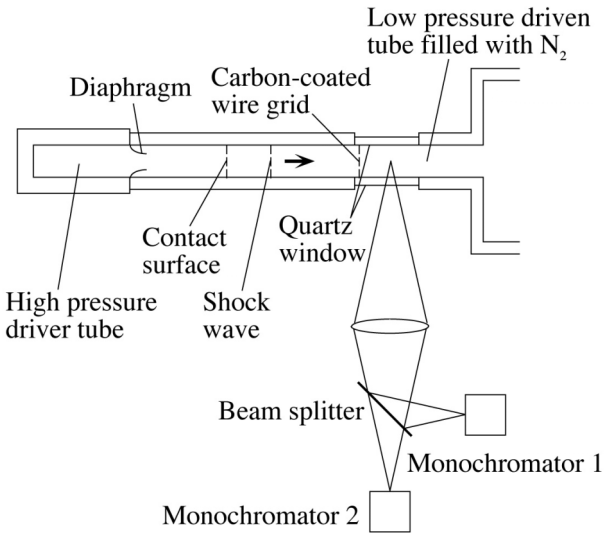

FIGURE 2. Schematic of experimental setup of Park and Bogdanoff [4].

SIMULATION PROCEDURE

The flow field around the carbon-coated wires is simulated using the DSMC method. The computational domain is half of the region between the two neighbor wires as shown in Fig. 4. The motions and collisions of neutral species are traced and, hence, time evolution of the flow fields is simulated. Simulated molecules are N, N_2, and CN. The computation region is divided into cells of the size as much as the mean free path of molecules and collisions between simulated molecules in the same cell are calculated stochastically. Figure 5 shows the cell network for the collision simulation.

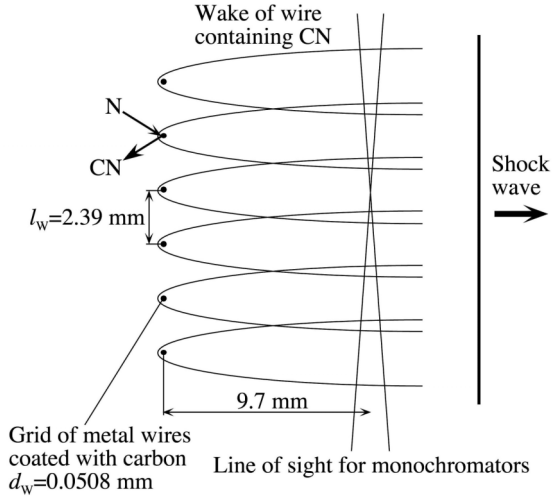

FIGURE 3. Schematic of the top view of the wake region of the wire grid [4].

TABLE 1. Computational Conditions

Temperature of incoming gas, N and N_2	7,060	K
Flow velocity of incoming gas, N and N_2	7,924	m/s
Partial pressure of incoming N	21,074	Pa
Partial pressure of incoming N_2	3,930	Pa
Temperature of carbon-coated wire	970	K
Diameter of molecule N_2	3.784×10^{-10}	m
Diameter of atom N	2.602×10^{-10}	m
Diameter of molecule CN	3.784×10^{-10}	m
Time step	2.0×10^{-10}	s

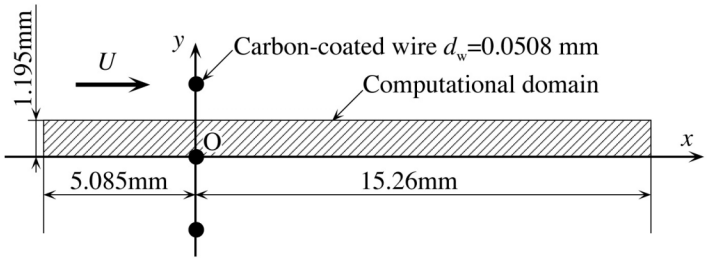

FIGURE 4. Schematic of the computational domain of the present simulation.

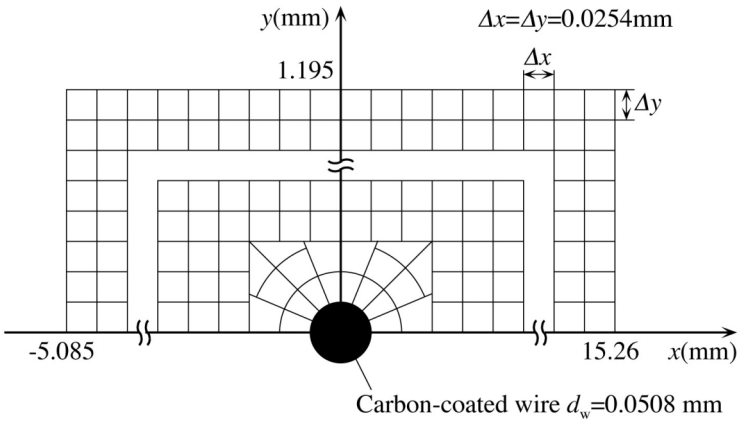

FIGURE 5. Schematic of the cell network for flow simulations using the DSMC method.

In the free motion stage of molecules, we consider influx of N and N_2 from the upstream boundary, collisions of simulated molecules with the carbon-coated wire, and efflux of simulated molecules. When a nitrogen atom collides with the carbon wall, the nitridation process (2) occurs with a probability P_n. The velocities of the reflected molecules are determined by using the diffusive reflection model with the wall temperature.

We consider six kinds of collisions between neutral species, i.e., N–N, N_2–N_2, CN–CN, N–N_2, N–CN and N_2–CN. The gaseous cyanogen molecules, CN, are produced only by the nitridation process (2). Therefore, the density of CN is much smaller than that of other species. If we use a common weight for all species, the number of simulated molecules with a lower number density will become small and hence the fluctuation of sampled data will become large. In order to suppress the fluctuation, we set the weight for CN much smaller than that for other species. The collisions between simulated molecules with different weights are treated by the weight algorism [6]. All molecules are regarded as a hard sphere. Collisions between simulated molecules are treated by using the maximal collision number method [6]. Table 1 shows the calculation conditions, which are determined from the results of Run No. 6 in Park and Bogdanoff's experiment [4]. Table 1 also shows the molecule diameters applied in this simulation and the time step. The diameters of N and CN, d_N are d_{CN}, are set at those of Ne and N_2, d_{Ne} are d_{N2}, respectively, because there is no data about these diameter. We discuss the effect of this assumption on our simulation results in the next section.

In the initial condition, there is no simulated molecule in the computational domain. At t=0, nearly totally dissociated nitrogen gas starts to flow into the computational domain from the left boundary. As time goes by, the flow field reaches the steady state. After that, we sample number densities, flow velocities, and temperature of all species.

RESULTS AND DISCUSSION

At first we show the typical simulation results for the case when the nitridation probability P_n is set at 0.1 for Run No.6 of Park and Bogdanoff's experiment [4]. Figures 6 and 7 show the number density distributions of N atom and CN molecule. Mach cones with carbon wires at the head are shown in Fig. 6. Figures 8 and 9 show the flow field of N atom and CN molecule around the carbon wire. Cyanogen molecules, CN, are generated on the carbon wires due to the impact of N atom. Cyanogen molecules do not spread out so much in the wake of the wires.

We vary the nitridation probability P_n. Figure 10 shows the relation between P_n and the CN concentration n_{CN} sampled at 9.7mm downstream of the wire, where n_N is the N concentration sampled at the same point. As P_n increases, CN concentration increases but saturates for large P_n. This feature shows that estimation of the nitridation probability using eq. (6) is invalid. Figure 10 also shows the relation in the case when d_N is set at $1.5d_{Ne}$ instead of d_N=d_{Ne}. In the case of large fraction of CN, the estimated nitridation probability largely changes depending on the assumed diameter d_{Ne}. However, for n_{CN}/n_N<0.005, the nitridation probability estimated using n_{CN}/n_N hardly differs regardless of the assumed diameter. In the present work, we treat only cases of small n_{CN}/n_N and, hence, assuming diameter of N and CN does not affect sensitively on our estimation.

Next question is why n_{CN}/n_N saturates against P_n. For example, even if P_n is increased from 0.1 to 0.5, n_{CN}/n_N increases only 2.2 times. Let us consider the generation rate R_{CN} of CN on the carbon wire, which n_{CN} is expected to be proportional to. Figure 11 shows the number density distribution of N atom around the carbon wire in case of P_n=0.1. The number density n_N of N atom becomes the maximum $n_{N,max}$ in front of the carbon wire. The same is said of the temperature T_N of N atom. The rate R_{CN} is proportional to $P_n n_{N,max}\sqrt{T_{N,max}}$, where $n_{N,max}$ and $T_{N,max}$ are the maximum values of the number density n_N and the temperature T_N of N atom. As P_n is increased from 0.1 to 0.5, $T_{N,max}$ is almost unchanged, about 25,000 K, but $n_{N,max}$ decreases from $2.1\text{x}10^{24}$ m^{-3} to $1.1\text{x}10^{24}$ m^{-3}. The rate R_{CN} is estimated to increases 2.6 times. This value roughly agrees with the increment of n_{CN}, 2.2 times. From this result, it is found that the increment of n_{CN} when P_n is increased is determined as a result of competition between increase of P_n and decrease of $n_{N,max}$. This is the reason of the saturation.

Lastly, let us reestimate of P_n estimated in Park and Bogdanoff's experiment [4]. They obtained P_n=0.190 for Run No. 6 measurement. We obtain n_{CN}/n_N=0.0040 by using eq. (6). The reestimated value of P_n becomes 0.136 using our simulation results. Figure 12 shows this procedure schematically.

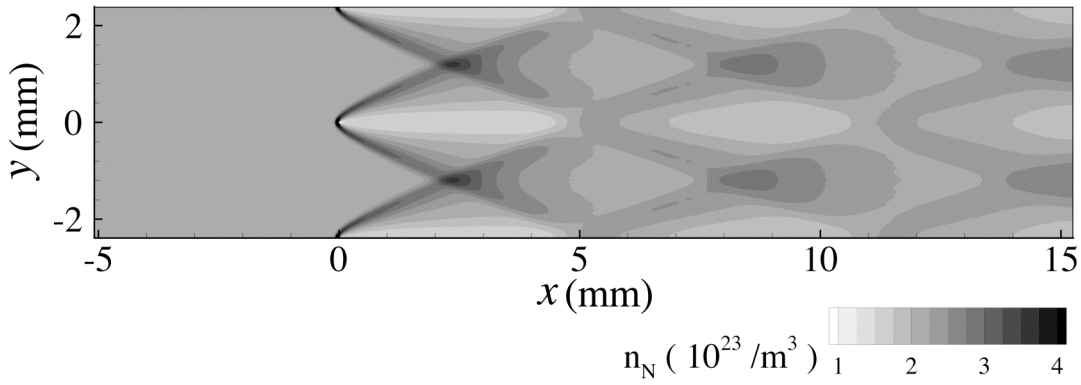

FIGURE 6. Number density distribution of N atom. (P_n is set at 0.1.)

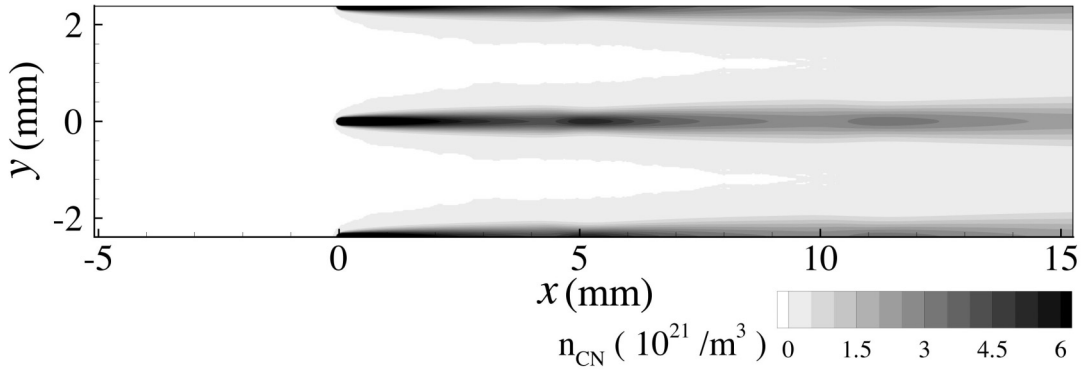

FIGURE 7. Number density distribution of CN molecule. (P_n is set at 0.1.)

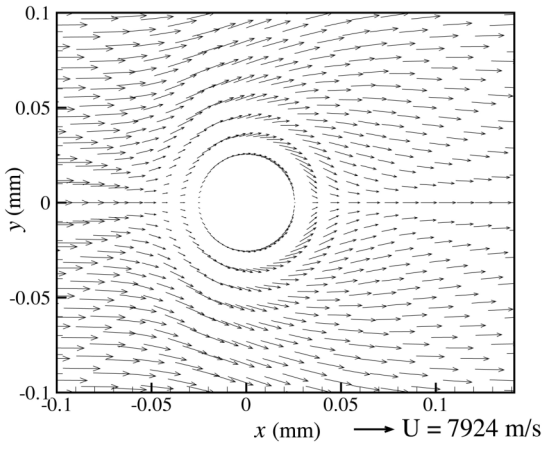

FIGURE 8. Flow velocity profile of N atom. (P_n is set at 0.1)

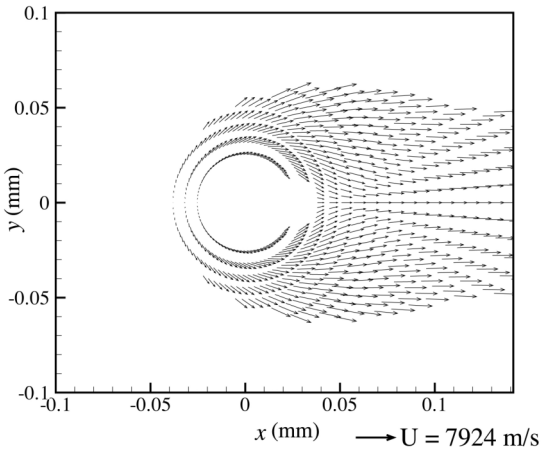

FIGURE 9. Flow velocity profile of CN molecule. (P_n is set at 0.1.)

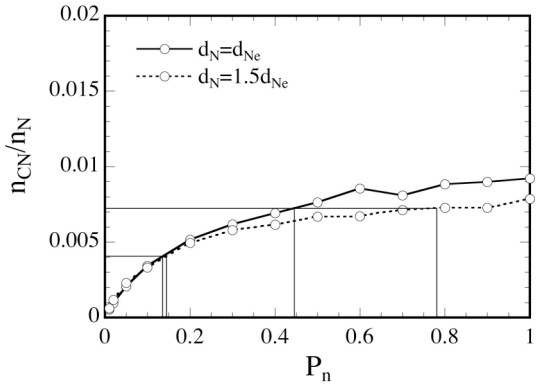

FIGURE 10. Relation between the nitridation probability P_n and the CN concentration.

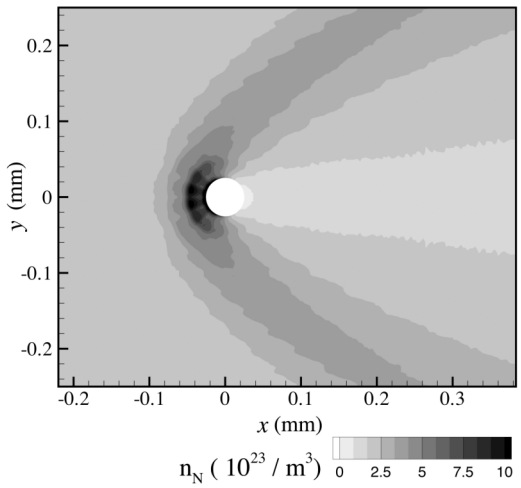

FIGURE 11. Number density distribution of N atom around the carbon wire. (P_n is set at 0.1.)

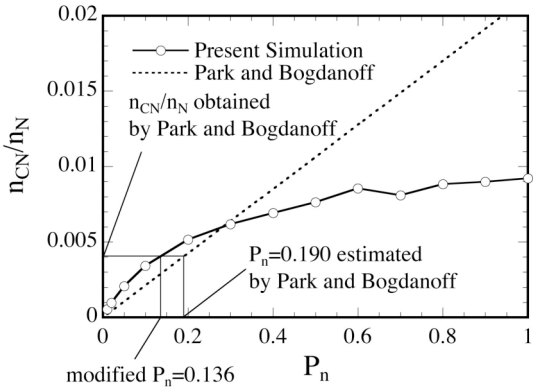

FIGURE 12. Estimation of the nitridation probability from the measured data of Park and Bogdanoff [4].

CONCLUSION

We reestimated the nitridation probability P_n measured in Park and Bogdanoff's experiment by performing DSMC simulation. The value of P_n obtained in their experiment was overestimated. The reestimated probability P_n for Run No. 6 of their experiment is corrected from 0.19 to 0.136.

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