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Technical Notes

Graphite Nitridation in Lower Surface Temperature Regime

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Nomenclature

A	=	surface area of graphite test piece, 1.524×10^{-3} m^2
k	=	surface reaction velocity, m/s
M_s	=	molecular weight of species s, kg/mol
R	=	universal gas constant, 8.314 J/(mol $\cdot$ K)
r	=	mass loss rate, m/s
T	=	temperature, K
α	=	reaction probability

Introduction

IN OUR previous study [1], the rate of nitridation reaction,

$$N + C(s) \rightarrow CN + 0.35\ \text{eV} \tag{1}$$

was studied through the heating tests in the inductively coupled plasma (ICP) heated wind tunnel. In the tests, a graphite rod with a diameter of 3 mm was exposed to a pure nitrogen test flow. The surface temperature of a graphite rod was measured during the heating test. The amount of mass loss was obtained by comparing the weight of the test piece between before and after heating. Obtained mass loss data were correlated to the rate of the nitridation reaction by using the following equation:

$$r = \frac{M_C}{M_N} A \rho_N k \tag{2}$$

where A and ρ_N denote the surface area of the graphite rod and atomic nitrogen density, respectively. The symbol k denotes the nitridation reaction velocity and is given by

$$k = \frac{\alpha}{4}\sqrt{\frac{8RT}{\pi M_N}} \tag{3}$$

where α denotes the reaction probability of nitridation. The reduced probability value of the nitridation reaction for the heating test condition was estimated, based on the measured temperature and mass loss rate of the graphite test piece. The number density of atomic nitrogen striking onto the graphite rod was calculated by using the computational fluid dynamics technique. The obtained probability values varied from 2.5×10^{-3} to 3.2×10^{-3} for the surface temperature, ranging from 1,822 to 2,184 K. The accuracy of the obtained value was examined by analyzing the heating tests fully theoretically and will be summarized in a separate paper [2].

The experimental data for the reaction probability are limited in the relatively high temperature regime. Based on the published works [3], the probability values were mainly reported for the surface temperatures higher than 1,800 K. The probability data will be needed in the lower temperature range of interest in the ablation of carbonaceous materials, typically less than 1,500 K. It is the purpose of the present study to provide the rate of nitridation through the heating tests, especially focusing on the lower surface temperature regime. Our previous approach, using a graphite rod, would not be suited to keep the surface of the heated graphite in lower temperatures, because the cross-sectional area of the test specimen exposed to the high temperature flows is very small. To meet the requirements of the surface temperature, two different types of test pieces are used: one has a larger diameter than that used in our previous study, and the other has a water cooling device additionally. By using these test pieces, the reduced probability value of nitridation is estimated, rendering as many approaches used in our previous study as possible, except for the heated test specimens.

Present Approach

The heating tests are carried out in the 110 kW ICP wind tunnel installed in the Japan Aerospace Exploration Agency (JAXA) by using the graphite test piece newly developed in this study. The amount of mass loss of the graphite test piece is obtained by comparing the weight between the before and after heating test. Obtained mass loss data are then correlated to the probability value of the nitridation reaction. Although the details of the experimental procedure are given in [1], the procedure is briefly explained next for completeness. The details of the facility specification and of the characterization studies on ICP flows can be found in [4,5].

To obtain the mass loss of the graphite test piece in the lower surface temperature regime, two different types of test pieces are developed in this study: one has a larger diameter than that used in our previous study, and the other is cooled by water. The schematics of these test pieces are shown in Figs. 1a and 1b. Hereafter, these test pieces are called type A and type B, respectively. Both types of test pieces consist of a flat-faced cylindrical graphite with a diameter of 30 mm and an axial length of 10 mm. The diameter of the graphite test piece used in this study is 10 times larger than that used in our previous work. The test piece is sustained by a sleeve made from graphite for type A and from copper for type B. For type B, the back face of the graphite test piece is cooled by water during the testing. The graphite test piece is fine carbon G530,§ manufactured by Tokai Carbon Co., Ltd. The density and the thermal conductivity are $1,820$ kg/m^3 and 104.0 W/(m $\cdot$ K), respectively, and the structure is isotropic. The surface area of graphite test piece before the heating test is 1.524×10^{-3} m^2; this value is the sum of the entire frontal surface of the graphite test piece, including its shoulder and side portions. The value will be used to evaluate the probability value of the nitridation reaction in this study.

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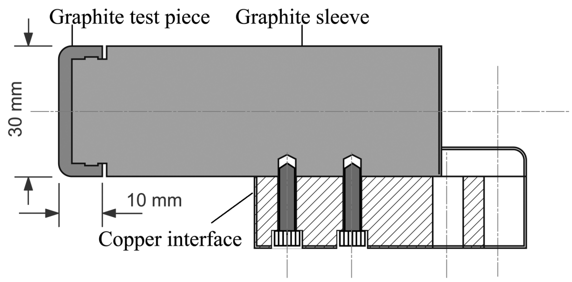
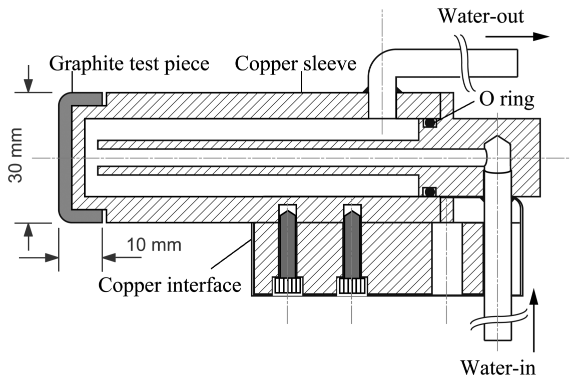
§Data available online at http://www.tokaicarbon.co.jp/en/products/fine_carbon/isotropic.html [retrieved 1 June 2007].



a) Type A



b) Type B

Fig. 1 Schematic of test pieces used in the heating tests.

In advance of the heating tests, the moisture content of the graphite test pieces is removed by heating the pieces in an inert gas environment at a constant temperature of 573 K for 3 h. After that, the graphite test piece is weighed by using an analytical balance (XS204, Mettler Toledo, Inc.), and is mounted on a sustaining sleeve. After the heating tests, the graphite test piece is removed from the sustaining sleeve, and it is weighed to obtain the amount of the mass loss of the graphite test piece.

An ambient gas in the test chamber is replaced by the nitrogen test gas three times before each of the wind-tunnel operations in order to reduce the amount of impurities remaining in the test chamber, such as oxygen. Recently, a radiation spectroscopic study was made to quantify the amount of impurities in the test chamber [4,5]. It was found from the study that the concentration of atomic oxygen could be reduced to less than 0.1% by conducting the replacement. It was also found from the recent theoretical study that the effect of such an amount of atomic oxygen to the mass loss data presented in this study was negligibly small [2].

Test conditions and the wind-tunnel operational parameters are summarized in Table 1. In this study, the heating tests are carried out by varying the working power of an induction coil and the exposure time. The working power used in this study ranges from 70 to 110 kW, and the mass flow rate of the working gas is 2 g/s, realizing a mass-averaged enthalpy ranging from 15 to 20 MJ/kg. The mass-averaged enthalpy values are determined by using an energy balance method.

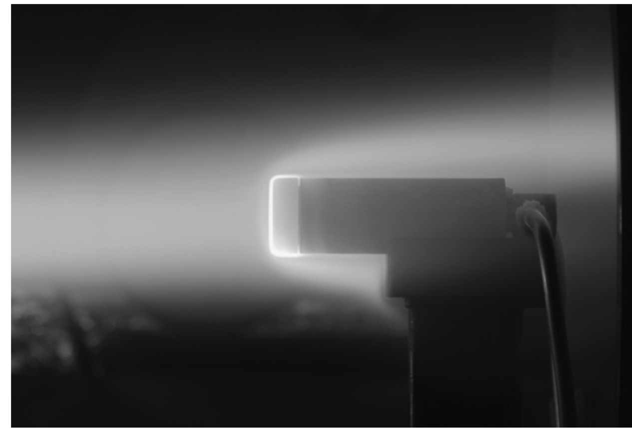


Fig. 2 Heating test of graphite test piece in the 110 kW ICP heated wind-tunnel facility in JAXA.

The forefront of the test piece is placed at 566 mm from the quartz tube exit. The surface temperature of the graphite test piece is measured by a one-color optical pyrometer. The emissivity value of the pyrometer was taken as 0.95 for all the heating tests conducted in this study. Because the temperature value would be proportional to the negative fourth root of emissivity, the accuracy of the measured surface temperature value was within 3% for the present temperature range of interest. A typical example of the operation is shown in Fig. 2.

To estimate the probability value of nitridation by using Eqs. (2) and (3), one needs to know the number density of atomic nitrogen striking onto the graphite surface. In this study, the density value of atomic nitrogen is determined by a numerical simulation, as was done in our previous study. In the numerical simulation, the flowfield over a graphite test piece is calculated by accounting for the ICP wind-tunnel freestream condition. The freestream condition is estimated by calculating the flowfield inside the plasma torch theoretically. The density values obtained for the present wind-tunnel test conditions are listed in Table 2. The details of the numerical methods can be found in [1,2].

Results and Discussions

Figure 3 shows the time histories of the measured surface temperature for all cases. One can see from the figure that the surface temperatures for type B are smaller than those for type A. In addition, the surface temperature increases with the working power for type A, whereas the difference in temperature is relatively small for type B. This trend is due to the fact that the graphite test pieces for type B are cooled by water during the testing. By enlarging the diameter of the test piece and water cooling, the surface temperature was 1300 K, which was lower than that obtained in a previous study by about 500 K.

As shown in this figure, the surface temperatures for all cases are nearly constant in time. Note that this trend is the same as that seen in our previous study [1]. A regression analysis is also made

Table 1 ICP wind-tunnel test conditions

Test piece		ICP wind-tunnel test conditions					
Type	No.	Working gas	Mass flow rate, g/s	Ambient pressure, kPa	Working power, kW	Enthalpy, MJ/kg	Exposure time, s
A	1	N_2	2.0	10.0	70	15	600
	2	N_2	2.0	10.0	70	15	1200
	3	N_2	2.0	10.0	90	18	600
	4	N_2	2.0	10.0	90	18	1200
	5	N_2	2.0	10.0	110	20	480
B	1	N_2	2.0	10.0	70	15	1200
	2	N_2	2.0	10.0	70	15	1800
	3	N_2	2.0	10.0	90	18	1200

Table 2 Mass loss data of graphite test pieces

Test piece type	Type A					Type B		
Test piece No.	1	2	3	4	5	1	2	3
Working power, kW	70		90		110	70		90
Density of N, $\times 10^{-4}$ kg/m^3	8.254		11.24		13.45	8.254		11.24
Duration time, s	600	1200	600	1200	480	1200	1800	1200
Surface temperature, K	1713	1723	1910	1901	2030	1372	1351	1399
Mass before heating, g	6.5499	6.5643	6.5632	6.5608	6.5564	6.652	6.4895	6.5017
Mass after heating, g	6.0096	5.2881	5.7191	4.8284	5.8037	5.9345	5.5505	5.4615
Mass loss, g	0.5403	1.2762	0.8441	1.7324	0.7527	0.7175	0.9390	1.0402
Mass loss, %	8.2490	19.442	12.861	26.405	11.480	10.786	14.470	15.999
Mass loss rate, $\times 10^{-4}$ kg/(m$^2 \cdot$ s)	5.9088	6.9783	9.2312	9.4729	10.290	3.9233	3.4230	5.6879
Reaction probability, 10^{-3}	2.0773	2.4462	2.2557	2.3208	2.0374	1.5410	1.3544	1.6234

based on the measured temperature data, and the results are presented in Table 2.

Because the surface temperatures are nearly constant in time during testing, the rate of mass loss of a graphite test piece is believed to be a linear function of time, except for the beginning of exposure. Thus, mass loss rates are calculated by dividing the measured mass losses by the exposure time. Obtained results are summarized in Table 2. Figure 4 shows the amount of mass loss of the graphite test piece as a function of exposure time. As shown in the figure, the amount of mass loss of the graphite test piece increases with the exposure time and the working power, as expected. Note that the amount of mass loss of the graphite test piece for type B is substantially smaller than that for type A. This difference is because the surface temperatures for type B are smaller than those for type A, as was shown in Fig. 3.

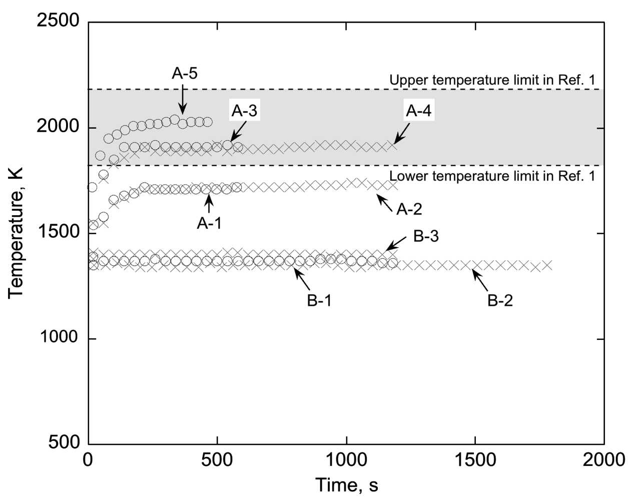


Fig. 3 Time variations of surface temperature of graphite test piece for all cases.

As was done in our previous study, the probability value of nitridation is estimated by using Eqs. (2) and (3) for each test piece. For the mass loss rate and the surface temperature, the measured values listed in Table 2 are used. As for the atomic nitrogen density, the deduced values listed in Table 2 are used. In Fig. 5, the obtained probability values for all the test pieces are plotted against the reciprocal temperature. Those values are also found in Table 2. The experimental uncertainty is estimated to be $\pm 5\%$ in the surface temperature and $\pm 15\%$ in the surface area. These uncertainties affect the reduced probability evaluated in this study by $\pm 17\%$. For the purpose of comparison, the probability values obtained in our previous study are also shown in the same figure. From the figure, one can see that the reduced probability of nitridation increases with the surface temperature and varies from 1.4×10^{-3} to 3.2×10^{-3} for the surface temperature, ranging from 1,351 to 2,184 K.

Based on the obtained probability values, a regression analysis is made, and the result is obtained in the Arrhenius form as follows:

$$\alpha = 8.441 \times 10^{-3} \exp\left(-\frac{2322}{T}\right) \tag{4}$$

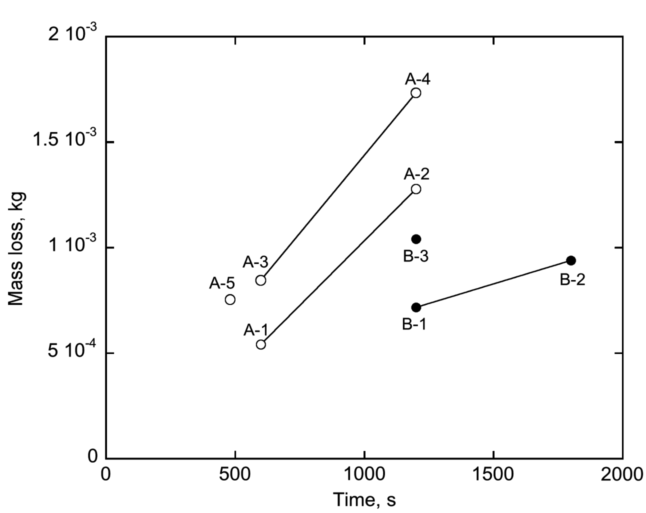


Fig. 4 Comparison of the amount of mass loss of the graphite test piece between different test conditions.

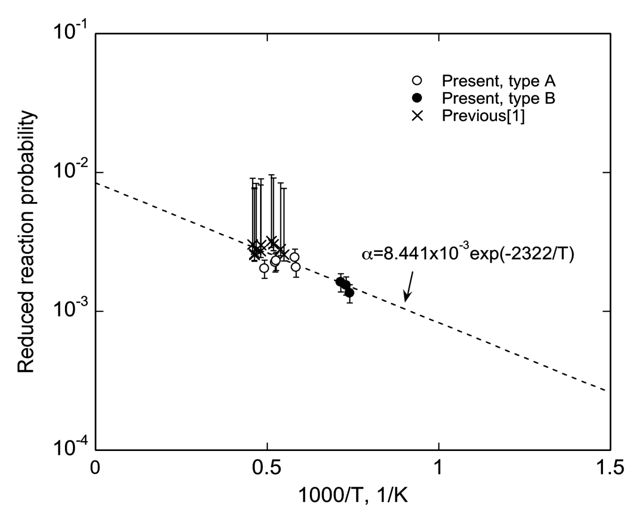


Fig. 5 Reduced probability values of nitridation for the present heating environment.

Conclusions

The obtained rate of the nitridation value becomes about 1.4×10^{-3} at the surface temperature of about 1,400 K and about 3.2×10^{-3} at about 2,200 K. Based on the obtained values, the numerical model of the nitridation reaction is proposed as the Arrhenius form.

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