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OXIDATION OF GRAPHITE WITH NEUTRAL OXYGEN ATOMS AT ELEVATED TEMPERATURE

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Abstract

Oxidation of pure electrolytic graphite with neutral oxygen atoms was studied experimentally. The source of oxygen atoms was weakly ionized highly dissociated oxygen plasma created in a microwave discharge at a power of 1 kW. Oxygen atom density was measured with a nickel catalytic probe and was $7.5\text{x}10^{21}\text{m}^{-3}$. Samples were exposed to plasma for different times. The loss of mass due to oxidation was about $5\text{x}10^{-4}$ g/s or 350 nm/s, and was independent from the treatment time. The samples were kept at the temperature of 800 K. Knowing the O-atom density in plasma and the etching rate allowed for calculation of the oxidation probability. At these experimental conditions it was about $9\text{x}10^{-3}$. The results indicate that interaction between graphite and oxygen atoms is not too aggressive even at such elevated temperature.

1. Introduction

The first wall material in many tokamaks is graphite. Graphite tends to be eroded by hydrogen ions during hot plasma pulses. The eroded material deposits on different walls and represent an unpredicted source of hydrogen. In order to avoid the hydrogen retention problem, the hydrogenated carbon deposits should be removed occasionally.

There are various methods for carbon removal but the simplest one is definitely oxidation. Any hydrogenated carbon is oxidized at elevated temperature, so the deposits are easy to remove. High temperature oxidation, however, cannot be performed on tokamaks. The problem with a rather high temperature is not only oxidation of metallic components, but also oxidation of the first wall material (graphite) itself. The required oxidation should be therefore very selective: we should remove hydrogenated carbon deposits while leaving the first wall material (graphite or CFC) intact. The most promising reagent is atomic oxygen.

Oxygen atoms are produced in electrical discharges. They interact with HC deposits forming volatile molecules like CO and OH which desorb from surfaces and are pumped away. Any discharge is suitable for generation of O atoms, but not all are that suitable for cleaning. One should always avoid plasma with a high electron temperature and/or high density. Not only energetic ions are not selective enough for etching, but the reaction products (CO in particular) tend to dissociate in plasma before pumped away. For generation of large quantities of O atoms, weakly ionized plasma with a low electron temperature performs much better.

2. Experimental system

Oxidation of graphite was studied using an experimental system shown in Figure 1. The system is pumped with a single stage oil rotary pump with a pumping speed of 16 m^3/h and an ultimate pressure of about 1 Pa. The discharge vessel is a glass tube with a diameter of 5 cm and a length of about 50 cm. Oxygen is leaked into the system through a precise leak valve with a flow controller. Experiments were performed at a pressure of 220 Pa. Plasma was generated by microwave generator at a power of 1000 W and a frequency of 2.45 MHz. The density of O atoms in plasma was measured with a nickel catalytic probe. Results of systematic measurements have been already reported [1]. Here we only state that the O-atom density (n_O) at 1000 W and 220 Pa is 7.5×10^{21} m^{-3}.

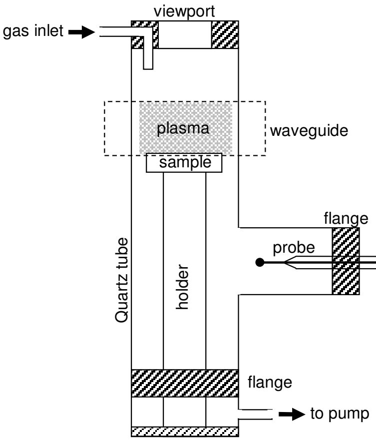

Fig. 1. Schematic of the experimental setup.

3. Oxidation of graphite samples

Samples were of disc shape with a diameter of 30 mm and a thickness of 5 mm. They were made from high purity pyrolitic graphite plates. The samples were kept in a dry atmosphere and weighted just before exposure to oxygen plasma. Samples were exposed to plasma for different time. The longest treatment time was 75 min (4500 s). The temperature increased rapidly after starting plasma treatment, but stabilized in few minutes to 800 K as measured by infrared camera Thermacam SC1000 by Flir Systems. After the treatment, the samples were weighted again. The mass of the samples versus the treatment time is plotted in Figure 2.

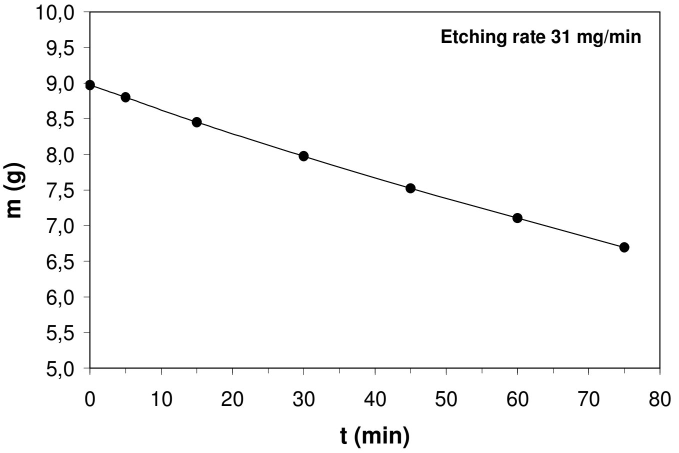

Fig. 2. Mass of graphite samples versus treatment time.

4. Discussion

The result presented in Figure 2 shows that the oxidation rate is constant. The loss of samples' mass is d(m)/d(t) = $5.1\text{x}10^{-4}$ g/s. The total volume of graphite etched is $V = S \times d = \Delta m/\rho$. Taking into account $\rho = 2.2$ g/cm^3, $\Delta m = 2.3$ g, total time t is 4500 s, we get for the etching rate $\varepsilon = d/t$=350 nm/s. Here, we took into account only etching on the upper plain of the disc. The lower part was embedded onto a holder and not exposed to plasma, while side etching may be neglected in the first approximation since the thickness of the disc is much smaller than the diameter. Taking into account the flux of oxygen atoms to the surface $j = ¼ n_0 v$ = $7.5\text{x}10^{21}$ m^{-3} x 630 nm/s = $1.2\text{x}10^{24}$ m^{-2}s^{-1}, the surface density of atoms $1\text{x}10^{19}$m^{-2} and the thickness of a carbon monolayer in graphite about 0.3 nm, one can calculate the etching probability $\eta = (\varepsilon/0.3)\text{x}10^{19}/j = 9\text{x}10^{-3}$.

Etching of graphite samples in our experimental system is therefore rather inefficient at 800 K. The reaction probability is only about $9\text{x}10^{-3}$, so only 1 oxygen atom out of 100 causes oxidation of carbon. This value is smaller than the etching probabilities for most polymers (except halogenated ones). Namely, as shown before [2], the etching probability of polymers may be higher than $9\text{x}10^{-3}$ even at room temperature, let alone 800 K. Graphite is therefore pretty immune to etching with oxygen atoms, at least up to elevated temperature.

Finally, it is worth mentioning that graphite can be oxidized also in molecular oxygen under equilibrium atmosphere, for instance in a furnace. In order to prove that our samples are etched by atoms and not only normal molecules, we placed some samples in a furnace in air at 800 K for 75 minutes. Samples were weighted before and after the experiment, and the loss weight was hardly measurable. It was orders of magnitude smaller that after oxidation in plasma. This is in sound with the other published results for oxidation of graphite exposed to air, pure O_2 gas and O_2 molecular beams [5-7]. It was found out that above ~ 1000 K there was relatively weak temperature dependence, while below, a strong decrease of erosion yields with decreasing temperature was observed. For example, at 800 K the erosion yield was only 10^{-6} C/O_2 [5].

5. Conclusion

Experiments on oxidation of graphite in highly non-equilibrium oxygen atmosphere were performed. The source of oxygen atoms was weakly ionized oxygen plasma at neutral gas pressure of 220 Pa. Plasma was generated with a microwave generator. At the power of 1000 W, the density of neutral oxygen atoms was 7.5×10^{21} m^{-3}, so the flux of atoms on the graphite surface exceeded 10^{24} $m^{-2}s^{-1}$. At these conditions, and the sample temperature of 800 K, the etching rate was about 350 nm/s. The oxidation probability was found to be rather low at 9×10^{-3}. The results of this experiment show that neutral oxygen atoms are rather inert to graphite even at elevated temperature, so the etching of hydrogenated carbon deposits can be performed without destroying the graphite first wall material too much.

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