GRAPHITE OXIDATION RATES IN COMPARISON TO REGIMES WITH APPLICATION TO THE OREGON STATE UNIVERSITY HIGH TEMPERATURE TEST FACILITY

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ABSTRACT

Understanding the phenomenon of oxidation in graphite at elevated temperatures is key for many nuclear engineering applications. This is due to graphite having extremely favorable material qualities for nuclear applications. Both analytical and empirical correlations have been suggested that describe graphite oxidation. These correlations require basic assumptions about the nature of graphite oxidation and divide graphite oxidation into four regimes, or areas where the rate of oxidation is significantly different and likely driven by different, or modified, processes.

Experiments were conducted for the construction of the Oregon State University (OSU) High Temperature Test facility (HTTF) where these underlying assumptions could be re-examined. This was done to understand how the graphite in the Oregon State University test facility will degrade over time and eventually fail. From these experiments it was investigated, and concluded, that the OSU HTTF will be able to complete its currently scheduled tests without failure in the test facility due to graphite oxidation.

In accordance with industry practices the oxidation behaviors of the graphite were investigated using thermos-gravimetric analysis (TGA). This analysis allows for the precise measurement of mass, temperature, mass change, temperature change, and gas volume flow. Simultaneously additional experiments were done involving a tube furnace that allowed for the macroscopic and qualitative inspection of the graphite.

The data from these tests was found to support the previously understood underlying assumptions in regimes not previously assumed. The data was analyzed to provide opportunities for further research in investigating graphite oxidation while specific oxidation rates in two of the regimes are reported for Tokai G-348 nuclear grade graphite.

KEYWORDS

Graphite Oxidation, Oxidation Regime, Diffusion rate, Combustions

1. INTRODUCTION

Carbon is a fundamental component of many important materials used for energy production today. Besides making up coal, which is burned for heat generation making up approximately 40% of energy produced in the world [1], it is also used for metallurgical processes, advanced materials such as graphene, and in nuclear applications as a neutron moderator.

In many of these applications graphite comes into contact with high temperatures and oxygen. These conditions cause graphite to oxidize. This oxidation is usually controlled through non-oxidizing coatings,

or through reducing the oxygen in the high-temperature environment. When these options are not available it is important to understand the intensity and extent of the oxidation for the safety of those involved. Particularly in nuclear reactors, graphite oxidation could potentially lead to the release of radioactive particles which must be minimized [2].

Because of its varied applications, graphite has been studied extensively especially in terms of oxidation. The Department of Energy (DOE) began research with attempts to form analytical or mathematical models to describe all oxidation [3]. However in subsequent studies that have taken place over the past fifty years, it was shown that a single model did not describe all behavior and that additional, empirical models were necessary depending on the application [4-11].

The DOE again released later notes to a mathematical model that was more select and simplified to key geometry that would be common in specifically nuclear applications [3]. The experiments whose data was included, while producing some agreement on the oxidation of graphite, produced a wide range of activation energies ($\approx 120 - 400 kJ/mol$) for the actual graphite oxidation [4,12,13].

This disagreement between experimental results led researchers to continue to examine the problem but with a larger account for grain structure, imperfections, and impurities in the graphite. This research also began to factor in oxygen transport rate vs. the oxidation rate to develop some very complicated relationships [14-18]. These relationships did agree on several outcomes that showed there was a relationship to the gradient of oxygen in the material depending on how close the diffusion rate of oxygen was to the rate of oxidation on the graphite surface.

To help classify this for the application most applicable to the upcoming design of high temperature gas reactors Xiaowei et al. [7] conducted experiments on graphite using similar assumptions of previous studies surrounding three oxidation regimes in graphite. Where in each regime the oxidation produces significantly different oxidation rates and activation energies, and the regime is mostly determined by temperature, but also by density, impurity level, and graphite microstructure. [19].

For the development of the Oregon State University (OSU) high temperature test facility (HTTF) it was necessary to know the oxidation rate of the graphite to be used (G-348 by Tokai Co.). Because some operating conditions are on the edge of the proposed regime temperature boundaries, it was also necessary to gain some understanding of which regime the oxidation would occur in.

The data here also provides more characterization of graphite oxidation for the specific graphite G-348 supplied by Tokai Co. Manufacturing. This is a high purity graphite that is commonly used for nuclear applications.

2. OUTLINE OF EXPERIMENTS

Three experiments were conducted and repeated using a thermo-gravimetric analysis (TGA) device. In each case a sample of the Tokai G-348 graphite was heated to the desired temperature so it could be compared with published literature.

The three test cases heated the graphite sample to an elevated temperature and then introduced gas with a known quantity of oxygen. The graphite was maintained at that temperature for up to an hour.

Stoichiometric equations were used, which are shown below, to predict the maximum oxidation rate and confirm the actual rate was within reason [2].

$$C + \frac{1}{2}O_2 \rightarrow CO \left(-111 \frac{kJ}{mole}\right) \quad (1)$$

$$C + O_2 \rightarrow CO_2 \left(-394 \frac{kJ}{mole}\right) \quad (2)$$

$$C + CO_2 \rightarrow 2CO \left(172 \frac{kJ}{mole}\right) \quad (3)$$

In each experiment a small graphite sample ($\approx 90\ mg$) was heated with a known gas present. The mass, flowrate, and temperature of the apparatus was then monitored with high precision to measure oxidation as it occurred to produce oxidation curves for the samples. This was done using a TGA device.

TGA involves using an apparatus that can take precise measurements of mass change, temperature, and temperature change usually while heating the test sample. TGA requires very small sample sizes. To satisfy this condition the graphite sample was machined to a small cube. While not consistent with the geometry of a high temperature gas reactor core, this analysis was the only tool available to OSU faculty and students to gain precise measurements of the graphite oxidation rates. For these experiments a Texas Instruments SDT Q 600 Thermo-gravimetric analyzer was used as shown in Figure 1.

Figure 1 Texas Instruments TGA Apparatus

Before each experiment conducted, as part of the experiments procedures, the TGA device was purged by heating to 1250℃. This purge cleans all trace elements off of the apparatus arms, and off of the crucibles used to hold the graphite samples. The crucibles are a high temperature aluminum oxide.

After the furnace has been purged and cooled, the furnace hood is open and the sample is loaded into the sample arm as shown in Figure 2.

The furnace is then closed and the experiment is conducted.

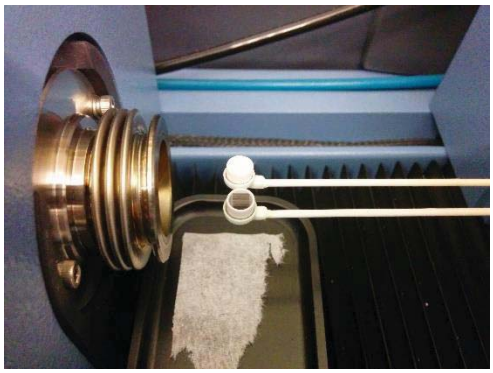

Figure 2 Loaded balance arms in the TGA Apparatus

2.1 Experiment 1

A sample of the graphite was prepared and placed in the TGA instrument which is heated to $1200^{\circ}C$ with an ingress gas of nitrogen. Once heated, the ingress gas was switched to standard purity helium with $< 5\ ppm$ oxygen (O_2) with a flow rate of 50 ml/min. The sample was held at these conditions until the helium was depleted with 40 ft^3 helium cylinder.

2.2 Experiment 2

A sample of the graphite was prepared and placed in the TGA instrument which is heated to $900^{\circ}C$ with an ingress gas of nitrogen. Once heated, the ingress gas was switched dry atmospheric air which contained approximately 21% (by mole fraction) oxygen with a flow rate of 50 ml/min. The sample was held at these conditions until the mass reached zero mg which took approximately 30 minutes.

2.3 Experiment 3

A sample of the graphite was prepared and placed in the TGA instrument which is heated to $1200^{\circ}C$ with an ingress gas of nitrogen. Once heated, the ingress gas was switched dry atmospheric air which contained approximately 21% (by mole fraction) oxygen with a flow rate of 50 ml/min. The sample was held at these conditions until the mass reached zero mg which took approximately 30 minutes.

3. RESULTS

In support of the HTTF test facility at OSU the experiments were conducted and the oxidation rates calculated and compared with the established oxidation rates for comparison. Xiawei's data was the most published and so the experiments herein were designed to be most comparable to his experiments [19].

Because the published data did not cover other gases, however, the results are separated into those that use atmospheric oxygen and those that use helium. Several anomalies occurred during experimentation that will be included with the results and discussed afterward.

3.1 Comparison of Atmospheric Oxidation Rates

The data was collected and used to form oxidation curves for the samples. A sample oxidation curve, of the mass, for a sample in the 1200℃ (experiment 3) is shown in Figure 3.

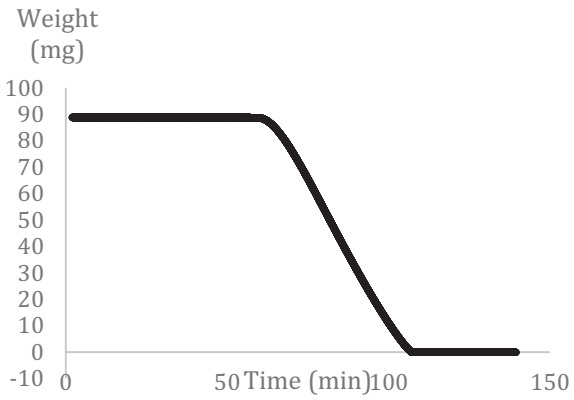

Figure 3 1200C Weight of sample for complete oxidation

In order to find the oxidation rate during oxidation the tails, where onset and completion of oxidation rate, are truncated. An example of the truncated curve is shown in Figure 4.

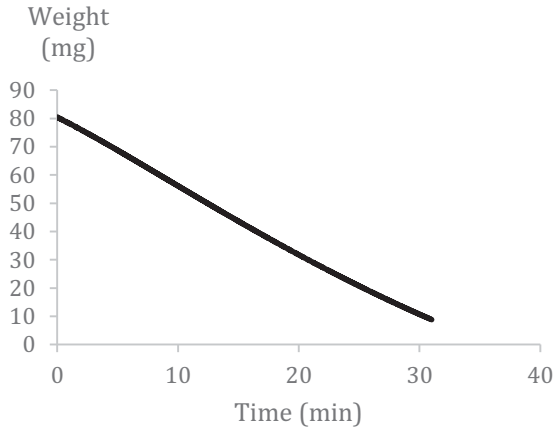

Figure 4 1200C Truncated weight of sample for complete oxidation

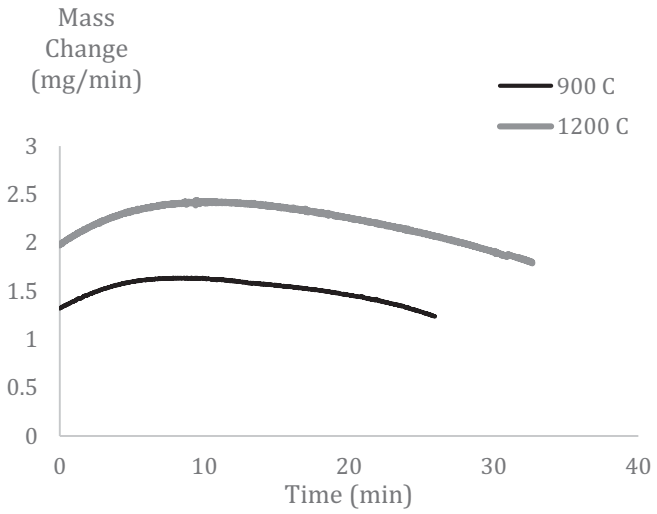

Figure 5 Average oxidation rate of sample over time

To compare to published data the average oxidation rate (mg/s), which is the slope of the line in Figure 4, was calculated and is shown below in **Table I**.

Table I Calculated Average Oxidation Rates

Source	Rate ($\mu g/s$)
900℃ Xiaowei	26
900℃ Experiment 2	25.2 ± 1.867
1200℃ Experiment 3	38.1 ± 3.019

For comparison purposes the average data from these results was plotted with published data to suggest that the data presented in these experiments is valid. The graph of the compared data is shown in Figure 6.

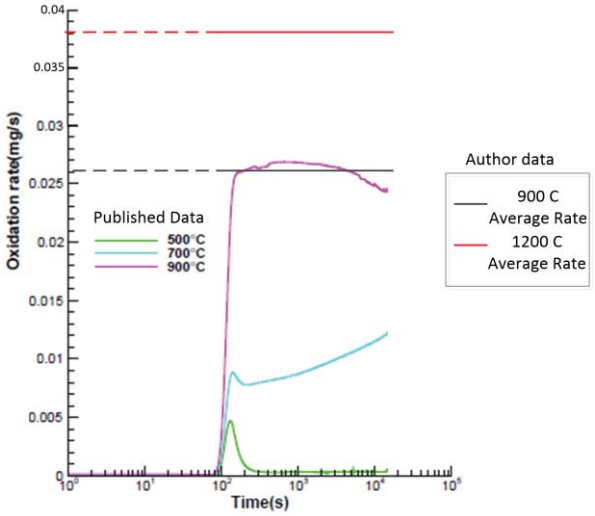

Figure 6 Collected data compared with published values [19]

3.2 Helium Oxidation Rate

After experiment 1 was conducted the oxidation rate for helium was established. Because it was desirable to extrapolate the data produced to the entire core, as literature suggested, both an overall oxidation rate and a percentage oxidation rate was found so that the expected lifetime of the OSU HTTF could be estimated.

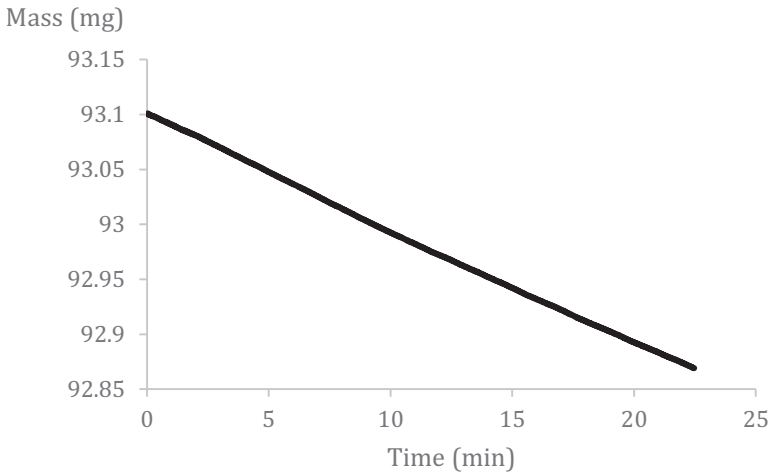

Figure 7 Weight of sample over time

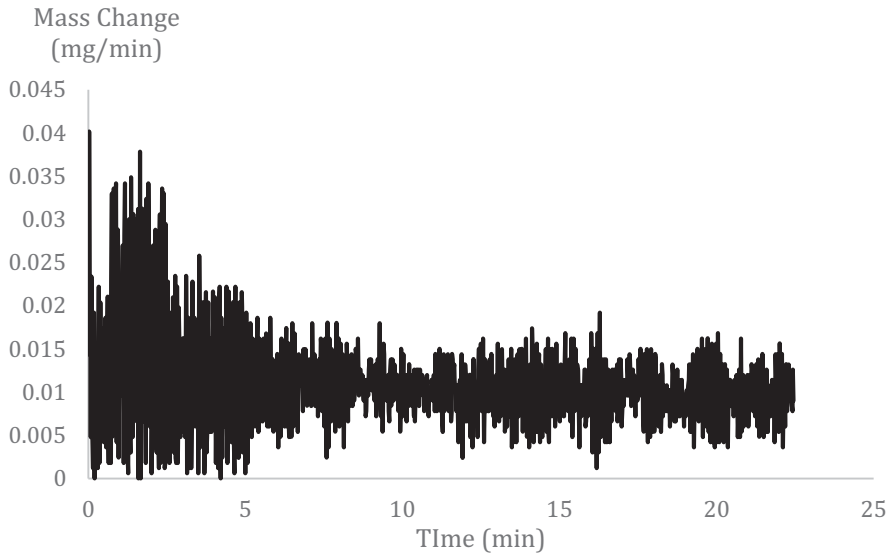

Figure 8 Oxidation rate of helium sample

By observance the oxidation rate of the sample is so small that measurement noise plays a significant role. However the error analysis will show that, while noisy, the oxidation rate still has a mean negative value where the sample is losing mass over time. This rate, and the mass change were then formatted in the form of mass loss by percent shown in Figure 9.

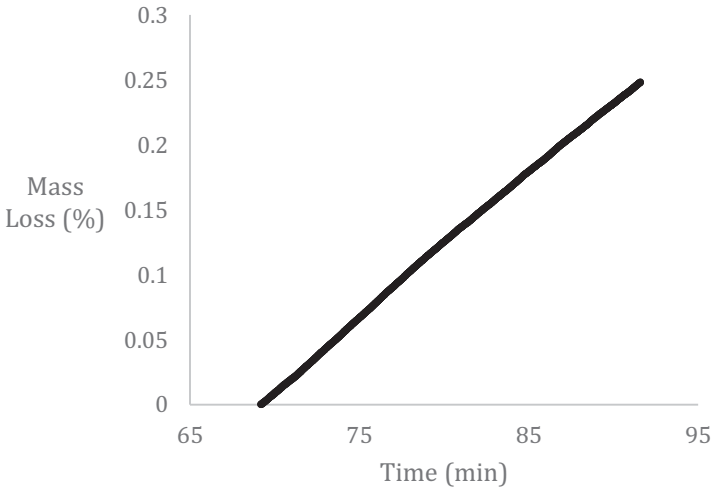

Figure 9 Mass loss percentage for graphite in a helium atmosphere

Summary values of the oxidation rate and percentage mass loss, with associated error, are shown in

Table II Calculated Average Oxidation Rates

Rate ($\mu g/s$)	Rate (%/min)
0.165 ± 0.049	$0.0106 \pm 3.19E-3$

4. DICUSSSION

4.1 Regime Identification

As shown by Figure 6 the oxidation rate that resulted from using the outlined procedures was very similar to that of other graphite oxidation experiments. This figure allows for confidence in the data and in the methods that the oxidation rate was taken accurately.

It should be noted that, even though the flow rate of gas in the above experiments was nearly double that given by Xiaowei [19], the oxidation rate was nearly identical in the case of 900C. This suggests that for a given geometry a flow rate can be achieved above which the oxidation rate does not increase. This leads to the assumption that the graphite used in this experiment experienced and immersed environment in the atmospheric gas where additional oxygen could not oxidize with the graphite. While no calculates were carried out to suggest how oxidation rates would be altered in a stagnant flow that relied on particle diffusion, it can be asserted that increasing the flow rate does not significantly increase oxidation rates after a certain point given a particular geometry.

4.2 Normal Operating Conditions & High Oxygen Ingress

One of the primary reasons this topic of graphite oxidation was researched by OSU is because of the construction of the HTTF there. This facility has a large portion of the core that is graphite and will be subjected $\approx 1000\ hrs.$ of test time with a temperature that is on the order of $1000℃$.

So that the effect that graphite would play on the power requirements for the duration of the testing. It was also necessary to understand that the graphite in the core would not fail before the testing was completed. The final design parameter of importance was that the test facility could run for a minimum of 1000 hrs. with less than 5% total graphite mass.

Inside of the test facility are also installed oxygen sensors at various locations within the flow loop. These sensors have a certain resolution and lower oxygen detection limit. Stoichiometric calculations were also carried out to ensure that if there was a leak sizeable enough to damage the core it would be detectable by the oxygen detectors.

The results from these analysis are not reported here because it is outside the scope of this paper, however the values obtained from the testing of the graphite for oxidation in the high-purity helium environment demonstrated that the design parameters of the facility, outlined above, should be met.

4.3 Error of Measurements

Error propagation was used in the case of determining the rates because both the statistical uncertainty and the error of the TGA analysis became a component of the overall error. The TGA apparatus has an error in calorimetric data of 2% [21]. This 2% error was applied for the measurements of mass at any point. While this error was evaluated, error bars were not included with the graphics because it made the graphs and images impossible to read due to the high rate of data acquisition.

4.4 Comparison to Xiaowei Experiments

Because the experiments in this paper were compared to the experiments some justification and outline of Xiaowei's experiments is necessary.

Xiaowei conducted oxidation experiments on Toyo IG-11 nuclear graphite. TGA was used with dry-air as the oxidation fluid at 20 ml/min. Oxidation rates were discovered for temperatures from $400℃ - 1200℃$ in $100℃$ increments however oxidation rate over time data was only provided for $500℃, 700℃, and\ 900℃$. The graphite in Xiaowei's experiments was machined graphite in small cylinders that fit into the TGA apparatus [4].

All experiments in this paper were designed to be as comparable to Xiaowei's to provide comparison in established literature. Unfortunately, due to manufacturer constraints and lack of information in Xiaowei's paper the geometry could not be exactly reproduced. In the DOE report on graphite oxidation it showed that, especially in low regimes, surface area and graphite oxidation are heavily dependent. However for larger temperatures and higher flow rates the oxidation becomes less dependent on surface area as macroscopic pores develop in the graphite. In the case of both Xiaowei's experiments and this paper, the graphite was assumed to be "submerged" in the fluid, this means that the graphite oxidation is not limited by the oxygen transport rate into the graphite [3]. It is because of this condition that the experiments between Xiaowei and this paper can be compared and are assumed reasonably equivalent.

5. CONCLUSIONS

The data presented from this experiment aligns well with published data for similar purity graphite. Hence the data here can likely be used as a benchmark for the oxidation rate of the specific graphite material Tokai G-348 graphite. The graphite tested appeared to fall in the high temperature regime ($>$ 900℃) suggested by Xiaowei [19].

Additional research should be done regarding graphite to increase the general knowledge of oxidation rates on the atomic level, however when a system is designed with graphite, the specific graphite used should be tested to form its own oxidation curve for the best understanding of the rate at which that graphite will oxidize.

As this practice has been applied to the OSU HTTF this experiment verifies that the original design with the attached oxygen sensors are sufficient in resolution to detect impure air ingresses that would damage the facility before the tests are completed. The helium gas selected also contains a low enough oxygen content that the overall oxidation of the facility due to testing is below the required limit.

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