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Informal Report

Performance of Carbon-Based Hot Frit Substrates

**2. Coating Performance Studies in Hydrogen
at Atmospheric Pressure**

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EXECUTIVE SUMMARY

The results of testing of coated graphite and both 2D and 3D carbon carbons are reported in this work. These samples have been tested with a two types of refractory carbide coatings, NbC and TaC. Most of the work reported herein has been conducted on TaC coated samples. Both coatings are produced using the same CVR process and were obtained from a single vendor.

Testing was performed under varying conditions of temperature and time. All tests have been conducted in a hydrogen atmosphere at approximately one atmosphere. Without a protective coating, any form of carbon erodes rapidly under these conditions. Certain metal carbide coatings can reduce the rates of attack by orders of magnitude provided that the coatings remain intact. Predicting the reliability of such coatings is a problem, because there is a large variability in the survival time of coatings before easily visible damage (e.g. spalling) occurs. Precise measurements of weight loss of the carbon substrates provide a method of quantifying the incipient failure of components at early stages before spalling is evident. Comparisons were made of the relative ability of various types of coating to protect each substrate from hydrogen attack. Based on these comparisons an operating lifetime for coated samples of less than 5 % weight loss of the carbon during the lifetime of the component was recommended.

This study found that the most effective combination of coating and substrate for high temperature duty in hydrogen was TaC deposited by the chemical vapor reaction method (Union Carbide) on AXF-5QI graphite. These materials withstood temperatures of 3000 K for as long as 2 hours, and showed no deleterious effects from multiple thermal cycles. The main questions that remain about this combination of materials are its mechanical strength at high temperatures and the effects of high pressure and flow rate of hydrogen on the erosion rates. For carbon-carbon components, superior performance from TaC-coatings can also be expected, for a limited number of cycles. These coatings were particularly effective for the first 5 minutes of exposure to hot hydrogen, during which no weight loss was observed. Coated carbon-carbon with a three-dimensional weave performed more consistently than did the two-dimensional woven materials.

Considerable effort was put into trying to detect an enhanced rate of erosion at intermediate temperatures (1400 K) as was found in the NERVA program. No such enhancement, i.e. "midband corrosion" was observed, and the temperature dependence of the reaction rates seemed to follow simple activated behavior consistent with a single rate-limiting process.

A number of conclusions have been drawn based upon the results of this study. These are as follows :

1. Conversion coatings are better than CVD coatings in protecting the carbon from hydrogen erosion.
2. Of the coatings tested, TaC CVR coatings provide the best protection from hot hydrogen.
3. Further evaluation of erosion rates needs to be performed as a function of pressure and flow rate of hydrogen.

4. For short duration applications with a small number of thermal cycles, coated carbon-carbon performance in hot hydrogen is quite good. Further, it may offer the advantage of strength over graphite.
5. For applications requiring long duration exposure to hot hydrogen with multiple thermal cycles, graphite is preferable to carbon-carbon, provided the mechanical strength is sufficient.
6. Optimization of the coating process for specific components should be done with tightly coupled feedback from the testing process.

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Performance of Carbon-Based Hot Frit Substrates

2. Coating Performance Studies in Hydrogen at Atmospheric Pressure*

1.0 INTRODUCTION

In the first report in this series¹ the results of testing of uncoated, carbon-based hot frit substrates in both helium and hydrogen were described. Additionally, that report outlined the procedures used for high temperature tests of samples in gases at atmospheric pressure. This report represents an extension of that work.

The substrates studied are similar to those discussed in Reference 1. In particular, graphite and both 2D and 3D carbon carbons have been used. These samples have been tested with a two types of refractory carbide coatings, NbC and TaC. Most of the work reported herein has been conducted on TaC coated samples. Both coatings are produced using the same process and were obtained from a single vendor, Union Carbide Corporation. The details of the samples and coatings are given in Section 2.

Testing was performed under varying conditions of temperature and time. All tests have been conducted in a hydrogen atmosphere at approximately one atmosphere. The results of all tests are presented in Section 3. These results as well as their implications are discussed in the subsequent two sections..

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2.0 EXPERIMENTAL

2.1 Materials

2.1.1 Gases

The two gases used in this work, helium and hydrogen, were obtained from Spectra Gases Inc. Helium was used as an outside cover gas between the susceptor and quartz jacket. Hydrogen was used as a test gas inside the susceptor (see Section 2.2). The helium was RG grade (99.9999 % purity). Prior to introduction into the induction furnace, the He was further purified by passing it through a tube full of calcium metal turnings which was kept at $\sim 650^{\circ}\text{C}$ for the removal of any residual oxygen and water from the gas. The hydrogen purity was 99.9995%. Before it was supplied to the susceptor the gas was further purified by passing through a liquid nitrogen-cooled coil containing molecular sieves and activated charcoal.

2.1.2 Substrates

2.1.2.1 Graphite

Data was obtained on samples fabricated from a purified grade of AXF-5Q which is denoted as AFX-5Q1. This material had been treated with chlorine gas to remove metals. The nominal sample size was a square 0.25" by 0.05" thick. The average initial surface area of these samples was $1.3 \pm 0.1 \text{ cm}^2$. In addition, a large amount of data was collected on unpurified graphite (AXF-5Q and AFX-5QC) since it was used as the base material for crucibles for the induction furnace. This data is not reported due to large differences in experimental configuration between samples and crucibles. Since the rate of erosion is dependent on geometry, comparisons must be made between samples placed in the same configuration, as far as possible.

2.1.2.2 Carbon-Carbon

Two types of carbon-carbon were tested. Both have been described in Reference 1. The first was from prototype hot frit material fabricated by Fiber Materials Incorporated (FMI) as a part of thermal hydraulic testing here at BNL. The woven material was either densified with pyrocarbon or left undensified. The initial dimensions of the uncoated specimens were nominally 0.245" x 0.253" x 0.09" and those for a coated test specimen were 0.249" x 0.250" x 0.093". Neglecting the laser drilled slots or pin holes present in each of the samples, the geometric surface areas of these samples were $\sim 1.4 \text{ cm}^2$.

The second type of carbon-carbon tested was obtained from Hercules and was a 3-D carbon-carbon weave. The samples were cylindrical in shape, measuring nominally 0.25" diameter by 0.25" high. Each sample had three small holes drilled lengthwise through it. The average surface area of samples before testing was $1.90 \pm 0.01 \text{ cm}^2$, neglecting these holes. This value was based upon the measurement of 5 uncoated samples.¹

2.1.3 Coatings

Two coatings were tested in this work. The bulk of the experiments was performed on samples which were coated with TaC. A more limited number was performed on samples coated with NbC. The coatings were applied to the various substrates by a single vendor, Union Carbide Corporation, Advanced Ceramics Division. The details of the coating process are held by the vendor to be proprietary, but it is a high temperature process in which the substrate provides the source of the carbon for the carbide. The metal comes from the decomposition on the heated carbon surface of a volatile metal chloride. For NbC and TaC deposition temperatures are in excess of 2000 °C.² The vendor refers to this coating process a chemical vapor reaction (CVR) process.

A detailed description of coatings obtained by this CVR process has been given previously.³ Figure 2.1 shows a TaC-coated graphite specimen. Typically, as in this figure, small holes in the coating can be seen. While the holes normally occur at the grain boundaries, they can occasionally be seen in the middle of grains. The adherence of the coating is described by the vendor as "tenacious"² and it is difficult to remove the as-received coating from the substrate without removing the portions of the substrate as well. The coatings applied in this manner are quite uniform in thickness and the coating readily penetrates pores and cracks in the sample. As noted in Reference 3, the coating process results in large, equiaxial grains in which a single grain is as deep as the coating thickness and mismatches between the thermal expansion coefficients of the substrate and coating can give rise to microcracking of the coating after cooling from the deposition temperature. The implications of this cracking will be discussed in Section 3.

²Union Carbide, Advanced Ceramics Division, Technical Information Bulletin, "Metal Carbide Coatings On Graphite : NbC, TaC, TiC, and ZrC"

³R. E. Barletta, P. E. Vanier, J. W. Adams, J. Svandrlk and J. R. Powell, FUEL-FRIT INTERACTION STUDIES, I. NET-1 Support Testing, October, 1991

Figure 2.1.. TaC coating on AXF-5QI graphite (1000 X).

2.2 Equipment

High temperature materials tests were conducted using a high frequency induction furnace under flowing gas conditions. The furnace design was based on a readily available RF generator and a system description has been given previously.³ An overview of the system is shown in Figure 2.2. The experiment was controlled by a Macintosh computer programmed using an interactive graphical package called LabView[®]. The controller was interfaced to the pyrometer output, the Lepel power supply and the gas handling system. This interface was described in Reference 3 and is shown schematically in Figure 2.3.

During the course of these experiments, modification of gas flow control was undertaken. For some of the tests conducted in this series the gas flow rate was measured by flowing it through calibrated gas rotameters. This system was changed, since the flow rates used in the experiments were at the lower end of the the settable range of these rotameters and due to variability in setting the flow rate between experiments. The rotameters were replaced with mass flow controllers obtained from MKS Instruments. These controllers had a maximum flow rate of 2000 sccm and one each was used to control the outer gas flow, inner inert gas flow and inner hydrogen flow. The two inner flows were set to 300 sccm while the outer flow was set to 1200 sccm. The gases for the inner flow were both connected to a 4-way valve which was operated using either manual or computer control (see Section 2.2.3). This valve allowed either gas to flow through the inner portion of the susceptor while the other gas was vented. Thus, flow rates for all gases could be established before starting the experiments and all gas lines adequately purged. During the heat-up phase of an experiment the inner flow was inert gas (He) this was

switched to hydrogen only when the sample was at the desired temperature changing the position of the 4-way valve.

Figure 2.2. Overall view of induction heater showing the outer quartz end fittings and rail arrangement.

Figure 2.3. Schematic of computer control for induction furnace experiments.

2.3 Temperature Measurement and Calibration

All temperatures were measured using an optical pyrometer which was focused onto the sample through the viewing hole in the susceptor, the window atop the quartz jacket and a front surface mirror. The pyrometer was calibrated with its associated optics (window and mirror) using an NBS-certified tungsten strip lamp in accordance with accepted procedures for pyrometer calibration as described in Reference 1. The analog output of the pyrometer was digitized, converted to temperature in Kelvin, and recorded by the Macintosh controller.

2.4 Test Procedure

Prior to each test, the sample and crucible were weighed. In addition, in some instances, a pre-test bakeout was performed by heating the samples in argon for 5 minutes at ~1230 K. Sample and crucible were again weighed. This later weight, which typically was less by a few milligrams than the unheated weight was used as the initial sample weight for subsequent heating tests. After weighing, the samples were placed in the crucible, the crucible placed in the susceptor (see Figure 2.4) and the sample purged with He for a minimum of 15 minutes at a flow rate of 1200 sccm and ~12 psig. The sample was then heated to the test temperature under helium purge (300 sccm inner flow), the pyrometer aligned and the temperature measured. Once the test temperature was reached, the hydrogen flow was established (300 sccm) and timing begun. Because of the difference in thermal conductivity between helium and hydrogen, a small correction was made to the applied rf power at the moment the hydrogen flow was switched on, so as to maintain a constant temperature. The magnitude of the correction, which corresponded to about a 20-50 K drop in temperature, was determined empirically as a function of temperature over a number of runs and later included in the program as a polynomial. The temperature was monitored for the duration of the test and recorded on disk. The test duration varied, but once it was completed the power was turned off and inert gas flow reestablished. A typical temperature profile for a heating cycle is shown in Figure 2.5. The sample was allowed to cool to room temperature before stopping the purge. The time of the test was recorded and the sample and crucible weighed. If another cycle was required, the procedure described above was repeated until the desired duration at temperature had been reached. Once sample heating was finished final measurements, weights and SEM inspection were conducted. In all cases, multiple weighings of samples and crucible were taken and the results averaged to give a weight at the completion of a cycle. Variations in weight of a few tenths of a milligram were common in the weighings. At the end of each cycle, the quartz tube and window were inspected and cleaned or replaced if necessary.

Figure 2.4. Typical arrangement of sample, crucible and susceptor. Sample - TaC-coated carbon-carbon; crucible - uncoated graphite (for clarity); susceptor - TaC-coated graphite.

Figure 2.5. Typical temperature profile during induction heating.

3.0 RESULTS

3.1 TaC Coatings

A large number of samples were coated in a single coating run (designated run A). These included samples of all substrate types discussed in Section 2.1.2. This run thus became effectively the reference TaC coating run for all the experiments on TaC reported herein. In addition a limited number of samples from a second coating run (run B) were tested to explore the effect of coating thickness as well as the run-to-run variability. Data on each of these coating runs is given in Table 3.1.

Run A coatings had a thickness of ~45 microns. All the as-received coatings had a silvery appearance. This is in marked contrast to the typical TaC coating which is gold in color. This is presumably due to a metal-rich surface, since pure Ta is silvery. However, a detailed study of cross sections of as-received samples using qualitative x-ray analysis revealed no evidence of a concentration gradient across the coating. Given the analytical tools at our disposal, it was not possible to determine either the bulk or local coating stoichiometry.

Table 3.1. Data on TaC coatings for hydrogen erosion testing

Designation	Nominal Thickness (microns)	As-Received Thickness (microns)	As- Received Appearance
A	60	45	silver
B	90	140-155	gold

3.1.1 Hercules Carbon-Carbon

All TaC-coated Hercules samples tested were from coating run A. Samples were tested at five temperatures 1400, 2300, 2500, 2800 and 3000 K. In one series of experiments, a single sample was heated at a given temperature for a number of heating cycles to determine the weight loss as a function of time. The results of experiment from this series of experiments are given in Figure 3.1 for a sample heated at 1400 and 2300 K and in Figure 3.2 for samples tested at the remaining three temperatures. The results in these two figures are expressed as percent of total carbon in the sample. Since the individual sample weights prior to coating were not known, an estimate of this value was made by weighing a number of uncoated samples. Based upon these measurements, an uncoated weight of 0.362 grams was assumed.

In a second series of experiments, a number of samples were heated in hydrogen to 3000 K. Each sample was heated for a different length of time and the weight loss observed for these samples are plotted in Figure 3.3 as the "Single Cycle" data set. Data from Figure 3.2 taken at the appropriate temperature are also shown in this figure for comparison as the data set "Multiple Cycle".

Figure 3.1 Weight loss from TaC-coated, 3D carbon-carbon (Hercules). Weight loss is expressed as % of original carbon in sample. A - 2300 K; B - 1400 K.

Figure 3.2 Weight loss from TaC-coated, 3D carbon-carbon (Hercules). Weight loss is expressed as % of original carbon in sample. A - 3000 K; B - 2800 K; C - 2500 K.

Figure 3.3 Weight loss from TaC-coated, 3D carbon-carbon (Hercules) at 3000 K for samples which had undergone either a single or multiple temperature cycle. Weight loss is expressed as % of original carbon in sample.

A third series consisted of heating a single sample in hydrogen cyclically between two temperatures. Each cycle consisted of two minutes at the low temperature followed by two minutes at the high temperature. Two experiments with two different sets of extrema were chosen. The high temperature extremum was the same 3000 K. In both experiments, a total of 20 cycles were run and the sample was exposed for a total 40 minutes in hydrogen at 3000 K. In one experiment, the low temperature extremum was set to a temperature well below the deposition temperature, 2000 K. A typical temperature history for a cycle and a half of this experiment is shown in Figure 3.4. Total sample weight loss in this experiment was 6.4% of the initial available carbon. In the second experiment, the lower extremum for the cycle was at or above the deposition temperature of the coating, 2500 K. Total sample weight loss in this experiment was 2.4% of the initial available carbon. Figure 3.5 shows this weight loss data expressed as a rate of carbon loss plotted as a function of temperature difference between the upper and lower cycling limits (3000 K).

Figure 3.4 Typical temperature profile of two high temperature and one low temperature portions of cyclic heating test. Time shown is relative to the start of the plot, not to the start of the cycling test. Temperature is expressed as a per cent of the upper set point temperature.

Figure 3.5 Results of thermal cycling tests expressed as the rate of carbon loss vs. the temperature difference between the upper test temperature and the lower set point

3.1.2 FMI Carbon-Carbon

A number of types of TaC-coated FMI-type samples were coated. In the first series, samples tested were from coating run A. Samples were tested at four temperatures 2300, 2500, 2800 and 3000 K. In one series of experiments, a single sample was heated at a given temperature for a number of heating cycles to determine the weight loss as a function of time. The FMI samples used in this series were either densified with PyC or undensified. These samples had a much lower weight prior to coating than the Hercules samples. As discussed above the uncoated weight for the Hercules samples was ~0.36 g. For the FMI samples, the uncoated weights for samples in these series were known. The PyC densified samples had weights in the range of 0.0923 ± 0.0088 g (based on the average of 24 samples), while the undensified samples had weights in the range of 0.1441 ± 0.0139 g (based on the average of 12 samples). Given the lighter weight of these samples (approximately a factor of 3), uncertainty in the weights (0.3 mg) during the experiments causes a larger scatter in the data for 2-d carbon-carbon samples than for the 3-d samples. This is particularly true for lower temperatures in which the incremental weight losses are quite small. Thus, although measurements were made of the weight loss at 2300 K, the scatter in the data rendered it useless.

Figure 3.6 shows weight loss from the samples discussed above at three temperatures, 2500, 2800 and 3000 K. The data in this figure represent experiments of a single sample at a given temperature. In particular, the sample shown in at 3000 K shows the lowest weight loss observed at that temperature, sample number FMI-TaC-5. In addition, to investigate sample-to-sample variation a number of specimens were run at 3000 K. The results of these experiments are shown in Table 3.2. As noted in the table spalling was observed in three of the four samples tested. An example of this is shown in Figure 3.7 (sample FMI-TaC-6).

Table 3.2. Weight loss from PyC densified FMI samples at 3000 K. All samples TaC coated in run "A".

Exposure Time (minutes)	Sample Number				Average Wt. Loss (%C)
	FMI-TaC-5 Wt. Loss (%C)	FMI-TaC-6 Wt. Loss (%C)	FMI-TaC-12 Wt. Loss (%C)	FMI-TaC-13 Wt. Loss (%C)	
2	-0.07	0.16	0.00	0.26	0.09 ± 0.15
5	-0.07	1.11	0.74	0.74	0.63 ± 0.50
10	0.73	2.26	3.97	3.35	2.58 ± 1.42
15	1.10	6.90	11.04 ^a	11.09 ^a	7.53 ± 4.72
20	2.84	14.87 ^a	-	-	8.86

^aWeight unreliable, sample spalling observed

Figure 3.6 Weight loss from TaC-coated, 2D carbon-carbon (FMI). Carbon-carbon was densified with PyC. Weight loss is expressed as % of original carbon in sample. A - 3000 K; B - 2800 K; C - 2500 K.

(a)

(b)

Figure 3.7 Detail of sample FMI-TaC-6. (a) As received. (b) After heating in hydrogen for 1200 seconds at 3000 K.

In a second series of experiments, undensified carbon-carbon samples were tested. These samples were also coated with TaC in run "A". Two temperatures were chosen for testing 2800 and 3000 K. Single samples were run at each temperature and the results are plotted in Figure 3.8.

Figure 3.8 Weight loss from TaC-coated, 2D carbon-carbon (FMI). Carbon-carbon was not densified. Weight loss is expressed as weight % of original carbon in sample. A - 2800 K; B - 3000 K.

The final series of tests on FMI samples involved tests on samples from other coating runs. This was done to test the run-to-run variability of the coating performance as well as to determine the effect of coating thickness on performance. Samples were tested from coating run "B" (see Table 3.1). In contrast to run "A", samples from this run were gold in appearance prior to heating as well as considerably thicker. Experiments were performed at 2800 K and 3000 K. The results of these tests are shown in Figure 3.9 for 2800 K and Figure 3.10 for 3000 K.

Figure 3.9 Weight loss from TaC-coated, 2D carbon-carbon (FMI) at 2800 K. Carbon-carbon was densified with PyC. Weight loss is expressed as weight % of original carbon in sample.

Figure 3.10 Weight loss from TaC-coated, 2D carbon-carbon (FMI) at 3000 K. Carbon-carbon was densified with PyC. Weight loss is expressed as weight % of original carbon in sample.

3.1.3 Graphite

In order to provide a baseline for the performance of the coated samples, uncoated AXF-5QI was also tested. The uncoated AXF-5QI was tested for two minutes in hydrogen at temperatures ranging from 3000 K to 2200 K. The weight loss data for these experiments is provided in Table 3.3. A second set of experiments was performed in which an uncoated sample was heated for a total of 4 hours at 1400 K in three successive heats. In this experiment sample weights were taken after each heating cycle. These data are also given in Table 3.3. In the testing performed at the higher temperatures, the hydrogen attack was not uniform over the surface of the sample. Etching of the graphite surface to a greater degree in the regions of the crucible holes was clearly evident. As the test temperature was decreased, these areas of increased attack became less and less pronounced.

Table 3.3. Weight loss from uncoated AXF-5QI heated in hydrogen.

Temperature (K)	Run No.	Time (minutes)	Weight loss (%C)
3000	1	2	3.7
2800	1	2	2.5
2600	1	2	0.91
2400	1	2	0.36
2200	1	2	0.16
1400	1	30	0
1400	2	90	0.08
1400	3	240	0.1

TaC coated samples of AXF-5QI were also included in run A. These samples were tested at three temperatures, 2500, 2800 and 3000 K. The weight losses observed for these samples are given in Table 3.4. It should be noted that the uncertainty in sample weighing of ± 0.0003 grams gives an uncertainty in the weight loss for AXF-5QI samples of approximately ± 0.18 % C. Thus, in most cases in Table 3.1, the weight gains reported are within the uncertainty of the measurement. The data given in Table 3.1 is also presented graphically in Figure 3.11 for runs at 3000 and 2500 K.

Table 3.4. Weight loss from TaC-coated AXF-5QI heated in hydrogen

Time (minutes)	Temperature (K)			
	3000		2800	2500
	Weight Loss (%C)			
	AXF-TaC-2	AXF-TaC-3	AXF-TaC-1	AXF-TaC-5
2	-0.06		-0.18	
5	-0.29		-0.08	
10	-0.13		-0.08	
15	-0.19			
20	-0.08		0.04	
25	-0.31			
30	0.08	0.04	-0.18	
35	-0.02			
40			-0.29	
45	-0.02			
50			-0.39	
60		0.43	-0.27	-0.08
65	0.27			
70			0.00	
80			0.11	
85	0.20			
90		0.57		
105	0.33			
120		0.71		0.02
125	0.62			
130			0.23	
160			0.54	
180				-0.06
240				0.06
300				0.14
360				0.08
420				0.25
480				0.14
540				0.25

Figure 3.11 Weight loss from TaC-coated AXF-5QI at (a) 3000 K and (b) 2500 K. Error bars represent uncertainty in weighing (see text). Data taken from Table 3.4 after 50 minutes (3000 K) and 105 minutes (2500 K).

3.2 NbC Coatings

A limited number of tests were run on NbC-coated 3-D carbon-carbon samples. Samples of NbC-coated carbon-carbon were obtained from Hercules. The sample size was the same as the TaC-coated samples described in Section 3.1.1 and an uncoated weight of 0.362 grams was assumed. The NbC was coated using the CVR process described in Section 2.1.3 and post heating examination revealed that the coatings were ~100 microns thick. Two samples were tested at two temperatures, 2300 K and 2800 K. The weight loss data from these tests are given in Figure 3.12.

Figure 3.12 Weight loss from NbC-coated 3D carbon-carbon at (a) 2300 K and (b) 2800 K.

4.0 DISCUSSION

The results presented in the preceding section provide information relevant to a number of issues regarding the efficacy of refractory carbide coatings, specifically TaC-coatings for the protection of graphite and carbon-carbon in a hydrogen atmosphere. The implications of these results will be discussed below, while more programmatic recommendations and conclusions will be presented in Section 5. Before discussing the implications of the data reported herein, however, it is necessary to qualify the discussion with a number of cautionary statements regarding the interpretation and general applicability of these results.

It should be noted, first of all, that the rates of attack given in the preceding section should not be viewed as absolute rates. Factors such as the effects of gas flow rate and impurities need to be explicitly investigated. Further, geometry effects could also play a significant role in affecting the rates of attack measured. In this work every effort has been made to make the measurements in pure hydrogen. It must be recognized that some interaction is bound to occur between the hydrogen and surfaces with which it comes in contact before reaching the test specimen. In particular, reaction products from these interactions could suppress the rate of attack on the sample. Tests at higher (and more relevant) flow rates could help to assess whether this is an important effect.

With respect to sample geometry, clearly each of the sample types tested had different geometries and surface areas. Estimates of the sample surface area based on geometric considerations alone (see Section 2.1.2) would imply that the surface areas of all samples were within a factor of two. But these estimates do not take into account surface irregularities, holes, slots, etc. Further, the substrate porosity should also be considered in estimating the surface area available for attack. This probably is very different for each of the substrate types tested.

A second caution in the application of these results concerns the type of coating tested. These results cannot be generalized to imply the performance of either NbC or TaC coatings which have been applied by methods other than CVR. Previous experimental work comparing the performance of CVD and CVR coatings revealed large differences in the performance between both coating types and coatings of the same type produced by different vendors.⁴ The ability of a given coating to provide protection of carbon-based substrates against hydrogen attack can only be evaluated on a case-by-case basis.

Extrapolating these results to situations of higher H_2 pressures and/or flow rates is a third area where care must be taken. The dependence of the rate of attack on these variables has not as yet been evaluated for coated samples, although future work in this area is planned. Comparison of these results with those obtained at much higher gas flow rates and pressures⁵

⁴R. E. Barletta, R. E. Davis, J. W. Adams, unreported results. These experiments were carried out in the experimental apparatus described in Reference 1. Some details of this work are given in Section 4.2.

⁵D. van Rooyen, work in progress.

indicate that corrections for pressure and flow rate could be small, but a much more systematic investigation of the effects of these variables needs to be performed.

Given these caveats, however, several important issues are in fact addressed by this study. These include the effects of cycling, temperature, coating and substrate type, sample-to-sample and run-to-run variability on the coating performance. Each of these areas will be discussed in more detail below.

4.1 TaC Coatings

4.1.1 Effect of Thermal Cycling

The effect of thermal cycling on coating performance seems to relate only to coatings on a carbon-carbon substrates, i.e. on substrates in which there is a large mismatch between coating and substrate CTE. For both the weaves tested, effects were seen as a result of thermal cycling. Table 3.2 shows evidence of the degradation of performance for TaC-coated 2-D carbon-carbon by an increase in the variation in the weight loss as a function of cycle number. In these experiments, cumulative time at temperature was accreted in a step-wise fashion, i.e. samples were cooled, weighed and then heated again. This increased the cracking in the samples, but since this process is stochastic the variation in the sample-to-sample performance increased.

Cycling was more directly addressed for 3-D carbon-carbon in two separate sets experiments. In the first, weight loss as a function of time was measured for samples in which a sample was exposed for a given time in multiple cycles as compared with individual samples exposed for that time with no cycling. It can be seen from Figure 3.3 cycling resulted in an increase in the rate of hydrogen attack by a factor of ~6.

The above discussion relates to cycling between room temperature and some elevated temperature. As the low temperature cycle point is raised, performance improves (see Figure 3.5). The intermediate temperatures shown were chosen to bracket the deposition temperature. It was found that, for low cycling above the deposition temperature, large improvements in performance can be achieved. Of course, as this low point is raised hydrogen attack at the low temperature will become an increasingly important component.

One may conclude several things from these thermal cycling experiments. First of all, thermal cycling appears to be important only for coated carbon-carbon. Thus, for applications requiring long life at high temperatures either graphite should be used as a substrate or the number of cycles should be minimal (≤ 3). For carbon-carbon, it is also beneficial to maintain an intermediate temperature during the cooler part of the duty cycle. The choice between graphite and carbon-carbon becomes a trade-off between mechanical properties and the thermal cycling required.

4.1.2 Sample-to-Sample and Run-to-Run Variability

Variability in sample performance seems, on the basis of this testing, to be a major issue with respect to carbon-carbon. Sample-to-sample variation between coatings on AXF-5QI substrates was quite small (see Table 3.4), whereas variation grew large as a function of cycling for the coated FMI samples from a single batch (see Table 3.2). This increase in variability is probably due to the stochastic nature of the coating cracking process. Batch-to-batch variation was also observed to be large (Figure 3.9). This could be in part due to the thicker coating for run "B". Samples from a number of similar coating runs would be necessary to investigate this variation more fully. It is interesting to note that the sample-to-sample variation for run "B" coatings was much smaller than for run "A". Further, no increase in variation with cycle number was noted in this coating. The existing data is not sufficient to adequately explain these effects. It points to the need for increased testing in this area, however.

4.1.3 Effect of Substrate

The most notable difference with respect to the effect of the substrate on coating performance was again between graphite and carbon-carbon. Long-term performance of coated AXF-5QI specimens was significantly better than for either of the coated carbon-carbon types tested. Again, the effect of CTE mis-match probably accounts for this. These differences are most easily shown by a comparison of the overall rate of weight loss as a function of temperature.

In order to make this comparison, estimates of the rate of hydrogen attack as a function of temperature is necessary. For TaC-coated graphite, this was quite easy, as the rate of attack at the three test temperatures appeared to be linear with time (see for example Figure 3.11). For the TaC-coated carbon-carbon samples, however, the data exhibited a short initial period in which no attack was seen. This incubation period is most obvious in Figure 3.2 for the 3-D carbon-carbon samples. At temperatures ranging from 2500 to 3000 K this period of no attack ranged from 5 to 10 minutes. This behavior was not observed for coated graphite although it is possible that the low rate of attack on these samples could have masked it. After this incubation period for TaC-coated carbon-carbon, the rate of hydrogen attack appears to be linear as with the coated graphite.

To compare the effect of substrate material, all the data used was from the run "A" batch. This eliminated any batch-to-batch variation. Data on carbon-carbon was selected to be beyond the incubation period discussed above, while for the coated graphite samples, only long-term data in which weight losses were above the 0.18 wt% detection limit were used. Using these selection criteria, the data were fitted using a linear regression analysis. The rates of H₂ attack was obtained from the slope of these fits and are given in Table 4.1 expressed as wt % C/cm²/minute. The rates were also plotted on a log scale vs. the reciprocal of the absolute temperature. The result is shown in Figure 4.1. It can be seen from this figure that the rates of the two types of carbon-carbon are nearly identical over a wide temperature range, while the rate of loss from the graphite substrate is significantly less.

Table 4.1. Rate of hydrogen attack on TaC-coated 2D-carbon-carbon, 3D-carbon-carbon and AXF-5QI graphite.

Temperature (K)	Rate (wt % C/cm ² /minute)		
	2D carbon-carbon	3D carbon-carbon	AXF-5QI graphite
2300	-	3.1×10^{-3}	-
2500	2.3×10^{-2}	1.7×10^{-2}	4.8×10^{-4}
2800	5.3×10^{-2}	3.5×10^{-2}	4.0×10^{-3}
3000	4.2×10^{-1}	2.4×10^{-1}	4.5×10^{-3}

Figure 4.1 Rate of weight loss from TaC-coated 2D and 3D carbon-carbon and AXF-5QI graphite.

4.1.4 "Mid-Band" Corrosion

Previous work on the NERVA reactor had indicated a peak in hydrogen corrosion at locations whose temperatures were much less than the peak reactor temperature⁶. This so-called "mid-band" peak was attributed to wide open cracks at lower temperatures which closed up at high temperatures because of the CTE mismatch between coating and substrate. The data given in Section 3.1.1 indicates that no increase in the rate of hydrogen attack occurs at temperatures in the vicinity of 1400 K even for systems with a large mismatch in the CTE between coating and substrate. Data taken out to 2 hours indicate no significant weight loss. This appears to be consistent with the Arrhenius rate behavior observed at higher temperatures. The rate data on TaC-coated 3D carbon-carbon plotted in Figure 4.1 gives the following temperature dependence for the rate of hydrogen attack

$$\log(\text{Rate}) = \log(6.5 \times 10^4) - \left(\frac{1.7 \times 10^4}{T} \right)$$

At 1400 K, this gives a rate of attack on the order of 10^{-7} %C/cm²/minute. For a sample size of the ones tested, this means that the amount of weight loss would be negligible for the times tested, as was seen in Figure 3.1. In fact, the above equation implies that a test lasting a week or more at 1400 K would be required to detect a weight loss greater than the uncertainty in the measurement.

4.2 Comparison of Coatings

4.2.1 TaC vs. NbC

Data in Section 3 allow for a comparison of coatings on a single substrate, 3D carbon-carbon. This comparison is shown at a single temperature, 2800 K, in Figure 4.2. Several things can be seen from this figure. First, the overall weight loss at any time is less for TaC-coated carbon-carbon than for NbC-coated carbon-carbon. After 30 minutes, this difference amounts to an increase of 40% in the amount of carbon lost. Secondly, one can note the rate of weight loss for the two types of samples. The rates of weight loss as evidenced by the slopes of the two curves are nearly identical once the TaC-coated sample begins to lose weight. This is probably more a measure of cracking in coated 3D carbon-carbon than anything else. Finally, and most importantly, the NbC coated sample does not have the same incubation period (with essentially no corrosion) which the TaC coated samples exhibit. At 2800 K, the incubation period is more than five minutes. This is particularly important for the short-term application of these coatings. During these early times (< 10 minutes), TaC coatings are vastly superior to the NbC coatings.

⁶see for example, A. J. Caputo NERVA Fuel Element Summary Report, July 1966 through June 1972, Y-1852, in 1973.

Figure 4.2 Comparison of TaC and NbC coatings on 3D carbon-carbon at 2800 K.

4.2.1 Effect of coatings

The data presented in this report when viewed as a whole indicate the superiority of CVR coating in general for the protection of carbon in a high temperature hydrogen environment. This point is most easily illustrated by a comparison of the rate data obtained on coated and uncoated graphite. Tests were run on both coated (TaC) and uncoated samples over a wide range of temperatures. The rate of weight loss from these samples was essentially linear. A simple Arrhenius plot in which the log of the rate loss is plotted against the reciprocal of the absolute temperature for coated and uncoated AXF-5QI is shown in Figure 4.3. It can be readily seen from this figure that coating results in an improvement in performance of roughly a factor of 400 at any temperature up to 3000 K.

These two sample types represent the extremes in performance measured. Obviously, changes in coating type would change the performance. It is further noteworthy that this analysis does not include the incubation period observed for TaC on carbon-carbon. Such an incubation period is not amenable to the simplistic analysis of the data shown in Figure 4.3.

The type of coating process used also has a profound effect on performance. Previous scoping experiments⁴ compared coatings of different types and deposition process on the same substrate. ZrC coatings were tested on undensified 2D carbon-carbon in hydrogen at 2900 K. The coatings were produced by both CVD and CVR processes. The CVD-produced coatings were obtained from Ultramet and Midland Materials Research, while the CVR coating was produced by Union Carbide. All three coatings were quite different in both their grain size and morphology as shown in Figures 4.4 - 4.6.

Heating in hydrogen produced profound changes in CVD coatings while the CVR coating remained relatively unchanged. Post heating photographs (Figures 4.7 - 4.9) show this clearly. In addition to the changes shown in these figures, changes in the Zr/C ratio were seen in the CVD coating from Ultramet.

Based upon these experiments in which little change in CVR coatings were seen in the temperature and times of interest (up to 20 minutes) and large changes were seen in the CVD coatings, it was concluded that CVR coatings would supply superior long-term protection. The experiments reported herein tend to confirm that fact. For TaC coatings, grain growth was not seen until very long times at high temperatures (typically ~60 minutes at 3000 K). While minimal coating changes do not guarantee improved protection, this seems like a plausible argument, since the adherence of the coating to the substrate is likely to decrease with changes in coating morphology, stoichiometry and grain size.

Figure 4.3 Rate of weight loss from TaC coated and uncoated AXF-5Q1 in hydrogen.

Figure 4.4 As-received ZrC, CVD coating from Ultramet. The substrate is undensified 2D carbon-carbon (3500 X). The grain size is on the order of 5 to 10 microns. Note the material in the grain boundaries and tetragonal appearance of the grains.

Figure 4.5 As-received ZrC, CVD coating from Midland Materials Research(1000 X). Substrate in undensified 2D carbon-carbon. The grain size is quite small ($\ll 10$ microns), and has a "cauliflower" appearance.

Figure 4.6 As-received ZrC, CVR coating from Union Carbide(200X). Substrate is undensified 2D carbon-carbon. The grain size is approximately 40 to 50 microns and the grains are extremely flat, following the substrate contour. Note the dark cracks in the coating along grain boundaries as well as holes in the coating. Most of the holes occur at the intersection of grains but some are in the middle of the grain.

Figure 4.7 ZrC, CVD coating from Ultramet after heating for 20 minutes in H_2 at 2900 K(3500 X). The substrate is undensified 2D carbon-carbon. Note the absence of material in the grain boundaries as well as the changes in the grain morphology.

Figure 4.8 ZrC, CVD coating from Midland Material Research after heating for 10 minutes in H_2 at 2900 K (1000 X). The substrate is undensified 2D carbon-carbon. In this sample the original grain structure (Figure 4.5) is absent. The underlying carbon-carbon is visible over most of the image as a cylindrical structure. The width of the fiber can be seen to be on the order of 3 microns. What remains of the ZrC coating is shown an open but connected structure on the left side of the photograph.

Figure 4.9 ZrC, CVR coating from Union Carbide after heating for 10 minutes in H_2 at 2900 K(200X). The substrate is undensified 2D carbon-carbon. Photograph is taken in the vicinity of a pinned hole which passes through the sample. There is little change in the coating. Grain size and morphology appear unchanged. There is some evidence of coating spalling in the vicinity of the crack which proceeds from the upper left portion of the photograph.

5.0 CONCLUSIONS

A large number of erosion tests have been performed on a variety of coated carbon specimens over a wide range of high temperatures, using relatively low flow rates of hydrogen at atmospheric pressure. Without a protective coating, any form of carbon erodes rapidly under these conditions. Certain metal carbide coatings can reduce the rates of attack by orders of magnitude provided that the coatings remain intact. Predicting the reliability of such coatings is a problem, because there is a large variability in the survival time of coatings before easily visible damage (e.g. spalling) occurs. Precise measurements of weight loss of the carbon substrates provide a method of quantifying the incipient failure of components at early stages before spalling is evident. During these early stages, the progression of the reactions with hydrogen is more predictable than in the later stages of rapid degradation. Comparisons can therefore be made of the relative ability of various types of coating to protect each substrate from hydrogen attack. The measured erosion rates are only relative, not absolute, and further experiments will be necessary to extend the conclusions to higher pressures and flow rates.

To define an operating lifetime for a coated carbon component in hot hydrogen based on these test results is difficult. The tests on 2D carbon-carbon generally showed spalling after about 5 % C weight loss. Once spalling occurs, of course, a sample can be expected to lose weight at a much faster rate. For a higher level of confidence in critical applications, it seems prudent to plan on allowing considerably less than 5 % weight loss of the carbon during the lifetime of the component.

This study found that the most effective combination of coating and substrate for high temperature duty in hydrogen was TaC deposited by the chemical vapor reaction method (Union Carbide) on AXF-5Q1 graphite. These materials withstood temperatures of 3000 K for as long as 2 hours, and showed no deleterious effects from multiple thermal cycles. The main questions that remain about this combination of materials are its mechanical strength at high temperatures and the effects of high pressure and flow rate of hydrogen on the erosion rates.

Carbon-carbon components are known to have greater mechanical strength than graphite at room temperature, and may offer improvements at high temperature also, though we are not aware that such tests have been documented. The best protection for carbon-carbon was also found to be a TaC CVR coating, although the survival times were not as long as for similarly coated graphite. These coatings were particularly effective for the first 5 minutes of exposure to hot hydrogen, during which no weight loss was observed. The performance of TaC for longer periods was also better than any other coating tested, especially if the part was heated only once, rather than for multiple thermal cycles. Coated carbon-carbon with a three-dimensional weave performed more consistently than did the two-dimensional woven materials.

Coatings of NbC were also tested, and found to offer better protection to carbon substrates than ZrC, but not as good protection as TaC. The traditional wisdom holds that Zr and Nb are desirable elements to use in nuclear environments, because of their relatively small capture cross-sections for neutrons. Ta has a much larger cross-section. This study shows that from the standpoint of survival in hot hydrogen, TaC coatings offer a significant advantage. In situations where neutron absorption can be tolerated without a major penalty, we recommend that TaC conversion coatings be used.

Considerable effort was put into trying to detect an enhanced rate of erosion at intermediate temperatures (1400 K) as was found in the NERVA program. No such enhancement, i.e. "midband corrosion" was observed, and the temperature dependence of the reaction rates seemed to follow simple activated behavior consistent with a single rate-limiting process. That process is assumed to be the thermal dissociation of adsorbed H₂ into H atoms.⁷

A number of serious questions remain unresolved. There is no fundamental explanation for the superiority of TaC over NbC and ZrC as a protective coating. There are only empirical comparisons between runs, of which there were only a few. Perhaps the NbC process could be improved to rival the performance of TaC. Perhaps the difference is merely a matter of impurity levels, rather than fundamental bond strengths or crystal structure. Perhaps it is a matter of stoichiometry, or gradients in stoichiometry. What processes occur during the "incubation period" of the TaC coatings? Is there structural damage without weight loss? Can a coating be made which will survive at even higher temperatures? For applications where neutron absorption is not crucial, perhaps alloys containing Hf might be useful. These questions can only be addressed by making many more coatings and applying sophisticated analytical techniques to study them. Unfortunately, the process parameters that go into the creation of vendor-produced coatings are not under the control of the end user, and are probably optimized for other criteria than those of interest to this program. There is at the moment little coupling between the assessment of coating performance and the production parameters of the next generation of coatings.

The results obtained in this study lead to the following conclusions and recommendations :

1. For applications requiring long duration exposure to hot hydrogen with multiple thermal cycles, graphite is preferable to carbon-carbon, provided the mechanical strength is sufficient.
2. For short duration applications with a small number of thermal cycles, coated carbon-carbon performance in hot hydrogen is quite good. Further, it may offer the advantage of strength over graphite.
3. Conversion(CVR) coatings are better than CVD coatings in protecting the carbon from hydrogen erosion. In particular of the coatings tested, TaC CVR coatings provide the best protection from hot hydrogen.

⁷J. T. Clarke and B. R. Fox, "Reaction of graphite filaments with hydrogen above 2000 K," J. Chem. Phys. **46**, 827 (1967)

4. Optimization of the coating process for specific components should be done with tightly coupled feedback from the testing process.

5. Further evaluation of erosion rates needs to be performed as a function of pressure and flow rate of hydrogen.

6. A statistical approach is necessary to assess the probability of failure of components. This means that large numbers of specimens must be tested. Also, for component development, larger coated objects should be tested, because the probability of failure probably increases with the size of the article.

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