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Westinghouse Astronuclear Laboratory

RESULTS OF A PRELIMINARY EXAMINATION OF THE HYDROGEN
CORROSION BEHAVIOR OF NbC COATED HIGH EXPANSION GRAPHITES

(Title Unclassified)

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Introduction

The hydrogen corrosion behavior of NbC coated, commercial grades of high expansion graphite was surveyed. It was thought that the thermal expansion properties of these materials would allow the retention of a crack-free coating over a wide range of temperatures. It was hoped that by this means the corrosion through cracked coatings⁽¹⁾ would be inhibited or eliminated.

The exploration of this idea was made the object of two concurrent programs. One survey of available high expansion graphites recently completed is the subject of this report. The second, more extensive program, is the development of high CTE graphites in NERVA fuel configuration from commercially available raw materials.⁽²⁾

Materials

Annular, 6 inch long, corrosion specimens were prepared from seven commercially produced high expansion graphites. The graphites selected represent three different manufacturing techniques and ranges of density, grain size, and coefficient of thermal expansion. ATJ graphite was used as a control material. All samples were coated with NbC, deposited from the vapor phase at 2100°C.

Basic information, descriptive of each of the graphites is presented in Table I. More detailed data are available in the references listed. Manufacturers' data on the properties of graphites which have not been extensively investigated at WANL are given in Appendix A. Photomicrographs illustrating

Table I - Characterization of Graphites Used

<u>Graphite</u>	<u>Max. Grain Size (mils)</u>	<u>Fabrication Method</u>	<u>Manufacturer</u>	<u>$\Delta l/l \times 10^3$ at 2000°C (in/in)</u>	<u>Ref.</u>
ATJ	6	Molded	Carbon Products Division Union Carbide Corporation	7.8 (WG) 10.3 (AG)	(4)
H-205-85	8	Molded*	Great Lakes Carbon Co.	11.4 (WG) 13.2 (AG)	(5)
A-175-S	3	Extruded*	Spear Carbon Company	11.2 (WG) 13.4 (AG)	(5)
EP-192 EP-1924 EP-192C	1	Isostatic Pressing**	POCO Graphite, Inc.	18.2 17.6 17.2	Appendix A
P-03	3	Molded	Pure Carbon Company	10.1 (radial) 10.0 (axial)	(6)
L-56	6	Molded	Pure Carbon Company	14.5 (WG) 14.0 (AG)	Appendix A

* These graphites underwent proprietary impregnation processes after graphitization. Subsequent heat treatment was limited to temperatures on the order of 1000°C.

** Final graphitization temperature of 2200°C. Other grades typically graphitized at 2800°C.

Figure 1 - Microstructure (135X) and Thermal Expansion of ATJ Graphite

Figure 2 - Microstructure (54X) and Thermal Expansion of A-205-85 Graphite

Figure 3 - Microstructure (80X) and Thermal Expansion of A-175-S Graphite

Figure 4 - Microstructure (135X) and Thermal Expansion of EP-192 Graphites

Figure 5 - Microstructure (135X) and Thermal Expansion of P-O3 Graphite

Figure 6 - Microstructure (135X) and Thermal Expansion of L-56 Graphite

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Figure 7 - Comparison of Thermal Expansion Data of Germane Materials

the micro-structures of the graphites and plots of their thermal expansion as a function of temperature are presented in Figures 1-6.

The reference curve used in Figure 1-6 is the thermal expansion characteristic of NbC as determined by x-ray techniques.⁽³⁾ The thermal expansion data already presented for individual graphites are combined in Figure 7 for purposes of comparison. Data for NbC and NERVA fuel are also plotted.

Apparatus and Procedure

The hydrogen corrosion test furnace is shown in cross section in Figure 8. It consists of a cold-wall pressure vessel water cooled end closures separated from the vessel by Micarta insulating rings, and a water-cooled, copper electrode introduced through a sliding seal. The hydrogen flows downward through the electrode into the furnace, and is exhausted through a channel in the base plate. The sample is held in graphite fixtures designed to mate with the electrode and with a depression in the base plate. The apparatus can accommodate a large variety of sample sizes and shapes by modification of the graphite fixtures.

A single sight port penetrates the pressure vessel to permit observation of the sample and optical temperature measurement. The graphite sample holders were adjusted to locate the maximum sample surface temperature in the field of the sight port. The ends of the samples were held in conduction cooled fixtures at temperatures considerably lower than the maximum.

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Figure 8 - Schematic of Hydrogen Corrosion Test Furnace

The end temperatures, estimated to be on the order of 200°-300°C, and the measured maximum temperature were the basis for the estimation of the temperature profiles along the sample. Corrosion profiles of uncoated graphite specimens also contributed to the estimates. The estimated temperature profiles for the three test conditions used are shown in Figure 9.

A standard operating procedure was followed in making the corrosion runs. The pressure vessel was pressurized with helium at 500 psig. A compressive load of 900 psi was applied to the sample through the sliding electrode to overcome the internal pressure and maintain adequate electrical contact. Hydrogen at 500 psig was passed through the interior of the sample. A small amount of hydrogen leaked into the pressure vessel outside the sample through the slip fit joints. The leakage made it necessary to have the exterior sample surface coated with NbC as well as the bores. Metallographic examination of corroded samples showed that the relatively small amount of hydrogen in the large (initially He filled) volume of the pressure vessel had a negligible effect on carbon loss as long as the external surface coating was intact.

With hydrogen flowing, the power was turned on. The sample surface temperature was brought to 1700°, 1900°, or 2300°C as measured by an I.D.L. "Pyro-Eye", two-color pyrometer. The test conditions were held for 4 hours unless the run was terminated sooner by sample failure.

The hydrogen flow rate was 200 scfh. In some of the first runs, 400 scfh, close to the maximum flow rate available with the equipment, was used. The weight losses were apparently independent of the flow rate

Figure 9 - Estimated Temperature Profiles for
Three Temperature Maxima

(for 400 and 200 cfh) within the experimental scatter.

Runs were terminated by power shut down followed by cooling in a flowing inert gas.

Results

The properties of each graphite determine a unique-crack structure in the deposited NbC coating. Photomicrographs of bore coat replicas, Figure 10, illustrate the variety of structures found with the graphites tested. It can be seen that the size and distribution of cracks varied from graphite to graphite. Some of the graphites permitted coatings with few or essentially no cracks.

The corrosion tested specimens were evaluated by weight loss, electrical resistivity change, and metallographic examination. The weight loss results are given in Table II.* The initial sample weight was of the order of 20-25 grams. The weight losses represent 4 or 5% of the initial weight; the scatter in the data is of the order of 1% of the initial weight. The differences in weight loss from graphite to graphite are also about 1% of the initial sample weight. Thus, the weight loss data do not indicate variations in corrosion performance.

* An analysis of NERVA fuel corrosion behavior was made.⁽²⁾ The calculation was adjusted for the geometry and thermal conditions of this report. The results indicated a weight loss of about 1 gram for the three temperature profiles. This is in reasonable agreement with the data given in Table II.

A. ATJ

B. P-03

C. H-205-85

D. A-175-S

E. L-56

F. EP-192

Figure 10 - Crack Structures in Coatings on Various Substrates-Photomicrographs of Replicas of Bore Coats 50X

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Table II
Non-isothermal Weight Loss of NbC Coated High
 Expansion Graphites from Hydrogen Corrosion

Graphite	$\Delta l/l \times 10^3$ At 2000°C (in/in)	Carbon Weight Loss in Grams ^(a) at Maximum Temp. of:		
		1700°C	1900°C	2300°C
ATJ (control)	7.8 (WG) 10.3 (AG)	0.46, 1.21	0.68	0.82
H-205-85	11.4 (WG) 13.2 (AG)	0.82, 0.82	0.74, 1.25	1.02
A-175-S	11.2 (WG) 13.4 (AG)	0.67, 1.18	1.91	0.71, 0.95
EP-192	18.2	(b)	(b)	(b)
EP-1924	17.6			
EP-192C	17.2			
P-03	10.1 (radial) 10.0 (axial)	0.91, 1.43	0.62	0.69, 0.70
L-56	14.5 (WG) 14.8 (AG)	0.72, 1.18	0.77, 0.99	1.11, 2.13 ^(b)
NERVA Fuel (Calculated)	10.9 (transverse) 8.9 (longitudinal)	~1	~1	~1

(a) Test time, 4 hours; H₂ pressure, 500 psig; and H₂ flow rate of 200-400 cfh.

(b) Severe corrosion at the external surfaces occurred as a result of outer coating splitting. Therefore, the weight loss data are not comparable to those of the other samples.

Various manifestations of corrosion were observed as functions of the local sample temperature. The same effects occurred, in general, in all samples, although they varied in appearance with the microstructure of the graphite. These are the same effects which have been observed in NERVA fuel elements. Figure 11 is a series of photomicrographs taken of a corrosion sample at points corresponding to temperatures up to 1900°C; the coating temperature was 2100°C. The effects are illustrated in P-03 graphite which has grain size and thermal expansion properties intermediate among the materials investigated.

Figure 11(a) is an example of the material in an uncorroded condition. Examples (b) through (h) demonstrate the establishment of a trend toward a narrowing of the affected zone with increasing temperature.

The lower temperature form of corrosion, first detectable in these experiments at 700°-800°C is a generalized dedensification (preferential binder corrosion) penetrating deeply into the graphite. This is observed as the enlargement of visible pores and the formation of new ones. The affected zone of graphite narrows and the pore size increases with increasing temperature in the 800°-1200°C range. The continuation of this trend is the formation of very large pores, or holes, in the graphite near the coating interface, and combination of the holes to form an interfacial gap. An explanation of these observations is presented in Appendix B.

Areas of severe local corrosion at coating cracks (corrosion rings) were found infrequently. In most instances, the generalized corrosion in the

B

D

F

H

A

C

E

G

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Figure 11 - Microstructure of Corroded P-03 Graphite as a
 Function of Local Sample Temperature, 100X

A. 600°C	E. 1400°
B. 850°	F. 1500°
C. 1150°	G. 1700°
D. 1300°	H. 1900°

- (A) GENERAL CORROSION-NO OBVIOUS
CONTRIBUTION FROM CRACKS
(HXG-1-215 - 5 1/2" 50X)

- (B) SELECTIVE CORROSION SUPERIMPOSED
ON GENERAL BASE
HXG-5-212C 5 5/16" 50X

- (C) SELECTIVE ATTACK AT CRACK -
CORROSION RING
HXG-1-214 - 2 3/4" - 1500 °C -
50X

FIGURE 12 CORROSION AT CRACKS

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a

b

Figure 13 - Incremental Electrical Resistivity Change

- a. High expansion graphite, maximum temperature = 2300°C.
- b. NERVA fuel element

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vicinity of a crack looked the same as the corrosion in regions of similar temperature without cracks. Occasionally, a microstructure was encountered showing local corrosion at a crack mouth superimposed on a base of generalized dedensification. The three observed types of corrosion behavior at cracks: generalized dedensification - no apparent contribution from the crack; crack attributable corrosion superimposed on general dedensification; and severe local corrosion at a crack, are illustrated in Figure 12.

The incremental change in electrical resistivity of a specimen was measured between two electrodes 1/2 inch apart. The measurements were taken at 1/8 inch increments along the length of the sample, before and after corrosion. A curve plotted from P-03 data in Figure 13 is given as typical of the various graphites tested. A typical plot of similar data from a NERVA fuel element is given for comparison.

It is significant that both curves have sharp maxima indicating high corrosion rates at positions corresponding to temperatures in the range 1000°-1400°C, and then indicate decreasing corrosion rate with increasing temperature. These phenomena in fuel elements have been attributed to the decrease in the size and number of differential CTE cracks as the coating deposition temperature is approached. However, the same phenomena are observed with high expansion graphite samples in which the size and number of differential CTE cracks is small or nil at any temperature.

Conclusions

Results are reported of an exploratory evaluation of the hydrogen corrosion behavior of NbC coated high expansion graphites. The preliminary results indicate no significant improvement in corrosion behavior with the use of high expansion graphite substrates. Further evaluation work on high expansion graphite substrates is recommended since the quality of the preliminary results do not justify the acceptance of this conclusion without reservation.

References

- (1) M. B. Blinn, "Hydrogen Corrosion Testing of NERVA Reference Fuel", WANL-TNR-129, September 16, 1963. (C-RD).
- (2) A. Boltax, "NRX-A6 Fuel Development Program", WANL-TME-1313, October, 1965. (C-RD)
- (3) C. R. Houska, "Thermal Expansion of Certain Group IV and V Carbides at High Temperature", J. American Ceramic Society, 47, No. 6, 310-311 (June, 1964).
- (4) V. Kachur, "Properties of ATJ Graphite", WANL-TME-956, November 4, 1964.
- (5) V. Kachur, "Structural Graphites with High Thermal Expansion", WANL-TME-891, September 9, 1964.
- (6) V. Kachur, "Properties of P-03 Graphite", WANL-TME-1031, January 12, 1965.

Appendix A

Properties^(a) of EP-192, EP-1924, EP-192C, and L-56 Graphites

	<u>EP-192</u>	<u>EP-1924</u>	<u>EP-192C</u>	<u>L-56</u>
Apparent density, g/cm ³	1.75	1.84	1.55	1.63
Anisotropy (unitless)	1.03	1.03	1.03	-
Electrical resistivity, ohm-in.	0.00098	0.00071	0.00142	-
Strength, psi				
compressive	16,500	20,000	10,000	16,000
transverse	-	-	-	6,500
flexural	10,000	14,000	4,000	-
tensile	3,500 ^(b)	4,800 ^(b)	1,800 ^(b)	5,000
Max. particle size, in.	0.001	0.001	0.001	0.006
Porosity, per cent	23	17	30	20
Modulus of elasticity	-	-	-	1.6 x 10 ⁻⁶

(a) This data taken from publications of the manufacturers.

(b) In house measurements indicate that these data are low.

Appendix B

The observed trend toward a narrowing of the corrosion affected zone of NbC coated graphite as a function of temperature can be explained by the competition between rates of chemical reaction and gas transport. The rate of chemical reaction is a strong function of temperature, while the transport rate, based on diffusion in pores, is proportional to temperature to a power that may vary from 1/2 to 1 depending on pore size. This effect would lead to a rapid rise in the chemical reaction rate over the 700°-1500°C temperature range as a consequence of the high gas pressure conditions of the experiments.*

A rudimentary quantitative description of reaction rates in pores can be based on work of Wheeler^(a). Assuming an idealized cylindrical pore of radius r , the overall rate of carbon loss, R_c is given by:

$$R_c = \frac{r}{2n/2} (2rkDC_0^{(n+1)})^{1/2} \text{ moles/unit area-unit time, where: } D \text{ is the}$$

diffusivity of H_2 into the pore, C_0 the concentration of H_2 at the pore mouth, n the order of the chemical reaction between C and H_2 , and k the chemical reaction rate constant. The depth of penetration of corrosion into the pore is given by: $X_m = 2^{n/2} \left(\frac{rD}{2k C_0^{(n-1)}} \right)^{1/2}$. From this it can be seen that as the chemical reaction rate increases with temperature the depth of penetration decreases while the overall reaction rate increases.

* There is also some evidence indicating that the chemical reaction is zero order with respect to H_2 pressure at about 600°C, and gradually approaches a first order dependence at about 1000°C - Breisacher and Marx, "The Hydrogen-Graphite Reaction Between 360° and 800°C", JACS, 1963, 85, pp. 3518-19.

(a) A. Wheeler, "Reaction Rates and Selectivity in Catalyst Pores", in Advances in Catalysis, 1951, III, Frankenburg, Kamarewsky, and Rideal ed., Academic Press, Inc., New York.

The observations make clear that hydrogen penetrates into the graphite and flows through the pores of the solid. The theoretical considerations suggest that in the regime of reaction in the pores (as opposed to reaction limited to the graphite-coating interface) the rates of chemical reaction and gas transport through the pores are controlling. In the temperature range below the temperature of maximum corrosion rate, the chemical reaction rate, which is very sensitive to increasing temperature, is probably the rate controlling process. It is likely that the maximum carbon loss rate corresponds to an approach to saturation of the gas phase in the graphite pores with hydrocarbons, and the decreasing carbon loss rate with further increasing temperature reflects the decreasing concentration of methane at equilibrium with carbon and hydrogen with increasing temperature. Under these conditions it is probable that gas transport in the pore structure of the graphite is the rate limiting process.

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