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THE EFFECT OF IRRADIATION
ON SILICONIZED-SILICON CARBIDE COATINGS FOR GRAPHITE

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INTRODUCTION

With increased interest in high-temperature, graphite-moderated, gas-cooled reactors, an important design problem has developed. Graphite is an excellent moderator material, but it reacts readily when exposed to oxidizing atmospheres at temperatures in excess of 400 C. To prevent the deterioration of the moderator, an inert gas, such as helium, if suitably purified, can be used for the coolant. However, if this approach is used no protection is offered if air comes in contact with the hot graphite, either accidentally or by inleakage. To protect against accidental oxidation, a protective coating for graphite has been proposed. This report summarizes the results of an investigation into the effect of irradiation on the quality and integrity of several commercial siliconized-silicon carbide (Si-SiC) coatings for graphite.

SUMMARY

Si-SiC-coated graphites have been oxidation-tested at 1000 C in air both before and after irradiation. Present data show that base graphites for coating must be fairly isotropic and must be stable toward high temperature radiation damage if the coating is to survive in-reactor conditions.

DESCRIPTION OF SAMPLES

The coatings used in this investigation were provided by three different manufacturers. The processes used to prepare them are proprietary, but they can be generally classed as Si-SiC coatings. Each manufacturer chose the particular base graphite that he preferred to coat.

The samples are coded according to the following system. The first number designates a particular type of graphite used as a coating base, the first letter is the manufacturer, and the last number is the

sample number assigned to the test. There are six graphite types and three manufacturers. Only one manufacturer (A) used two coating methods and, although the data are included for both, only one is being produced commercially.

EXPERIMENTAL METHOD

Some of the samples from each manufacturer were selected at random and given a pre-irradiation oxidation test at 1000 C in flowing air. The results are in Table I. These samples, along with some untested ones, were loaded into a graphite boat and charged in an irradiation facility. They were irradiated in a helium-CO₂ atmosphere at about 500 C, and received approximately 8×10^{20} nvt ($\bar{E} > 1$ mev) exposure. After removal from the reactor, they were heated to 1000 C in flowing air and weighed periodically to determine any weight changes. Weight loss was used as an index of coating failure. The results of these tests are in Table II. The base graphites used for the coatings were irradiated at the same time and the effects are shown in Table III.

TABLE I

OXIDATION OF UNIRRADIATED Si-SiC COATINGS
IN 1000 C AIR

<u>Sample Code</u>	<u>Time (Hours)</u>	<u>Weight Change (Per Cent)</u>	<u>Visual Appearance</u>
1A-2	169	-0.0017	good
2A-3	142	-0.0014	good
3B-6	162	-0.0044	good
4C-3	161	+0.199	good
5C-7	24	-2.06	cracked
6C-8	46	-1.26	good

TABLE II
OXIDATION OF IRRADIATED Si-SiC
COATINGS IN 1000 C AIR

<u>Sample Code</u>	<u>Time (Hours)</u>	<u>Weight Change (Per Cent)</u>	<u>Remarks</u>
1A-1	158	-5.5×10^{-3}	
1A-2	294	-2.8×10^{-3}	
1A-5	396	-23.5	Failed
2A-3	124	-22.9	Failed
2A-4	577	-4.4×10^{-2}	
3B-1	244	-1.45×10^{-2}	
3B-2	244	-8.0×10^{-3}	
3B-3	124	-9.1	Failed
3B-4	244	-4.6×10^{-3}	
3B-5	244	$+2.7 \times 10^{-3}$	
3B-6	493	-4.4×10^{-4}	
3B-7	493	$+1.8 \times 10^{-3}$	
3B-8	493	-3.9×10^{-3}	
3B-9	493	-1.0×10^{-3}	
4C-1	276	-.13	Failed
4C-2	128	$+1.2 \times 10^{-2}$	
4C-3	128	-3.0×10^{-2}	
4C-4	192	-16.7	Failed
4C-5	192	$+6.4 \times 10^{-2}$	
4C-6	192	-4.5	Failed
5C-10	265	-1.9	Failed
6C-9	265	-1.8	Failed

TABLE III
EFFECT OF IRRADIATION ON CANDIDATE
BASE GRAPHITES FOR COATING

Graphite Type	Length Change Per Cent	Crystal Parameters					
		$C_o A$ Before Irradiation	$\Delta C_o A$	$L_c A$ Before Irradiation	$\Delta L_c A$	$L_a A$ Before Irradiation	$\Delta L_a A$
1*	+0.023	6.740	+0.012	350	-30	400	-120
2*	-0.182	6.766	+0.014	193	+19	330	-130
3(II)	-0.034	6.734	+0.002	410	-30	490	-130
3(I)	+0.007	6.721	+0.012	475	-85	470	-10
4*	-0.282	6.805	-0.011	147	+11	270	-90
5*	-0.060	6.741	-0.001	380	-85	680	-440
6*	---	6.721	+0.015	395	+5	490	-220

*Orientation of pieces unknown

DISCUSSION

The samples were inspected visually for cracks and defects that would indicate a poor coating. Sample 5C-7 had one crack running parallel to the long axis of the sample. Not all the samples placed in-reactor were given a pre-oxidation test, but all were inspected visually and appeared completely coated and without cracks. As can be seen from Table I, samples from manufacturer A using graphites 1 and 2, and samples from manufacturer B using graphite 3, showed practically no weight change during pre-irradiation oxidation. Manufacturer C's coating on graphite 4 had a weight gain, but remained crack-free. The weight gain associated with manufacturer C's coating is probably due to the oxidation of the free silicon in the coating to form SiO_2 .

In addition to the oxidation test, some of the samples were sectioned and polished using standard metallographic techniques (Figures 1-3). These samples in the photographs were cut from cylindrical specimens

and show sections of the long side, a rounded corner and the end of the rod. The dark grey mass at the top of the photomicrograph is the resin used to hold the specimen. The grey and white layer is the coating and the bottom dark grey is the graphite substrate. In the coating layer, the grey is interpreted as SiC and the white as silicon. It is interesting to note the partial penetration of the coating into the substrate and also the variation in thickness on the rounded corners. It is difficult, if not impossible, to get good continuous coatings on sharp edges.

Post-Irradiation Testing

After irradiation, the samples were subjected to 1000 C flowing air to determine if the protective quality of the coating had been affected. An analysis of the data in Table II brings several facts to light.

Manufacturer A's coatings had been prepared using two graphite types and, in addition, two coating methods. Manufacturer A said, when preparing the samples, that the coating method used on samples 1A-1, 1A-2 and 2A-4 was his preferred coating. The data indicate that this preference is well founded. It is significant that samples 2A-3 and 1A-2 had been given an oxidation test prior to irradiation and remained crack-free, yet 2A-3 failed the identical oxidation test after irradiation.

An excellent example of what can happen to a coated graphite body when only a small crack is present is shown in Figure 4. This is a section of sample 2A-3 that showed a considerable weight loss. The sample was inspected visually after irradiation and before oxidation; no visible defects were apparent. After the oxidation test the sample was again inspected with a stereo microscope. There were no detectable cracks but a small pit in one corner was observed. The sample was then mounted and sectioned, showing the erosion. The coating remained fairly continuous and the substrate oxidized away leaving a large void space. A point of interest is the manner in which oxidation took place, leaving a flat surface normal to the long axis of the sample.

Manufacturer B's samples were applied to graphite type 3 using, as far as is known, a single method of coating. Except for one sample, 3B-3, all survived.

Manufacturer C's coating allowed a comparison of three different substrate types using a single coating method. Pre-irradiation testing was not conclusive, but suggested graphite substrate type 4 was the best of the three. Post-irradiation testing indicates that none of these three graphites are satisfactory as coating bases when subjected to irradiation.

Base Graphites for Coating

Table III lists the effects of irradiation on the different graphite types that were coated. Although those data are based on a limited number of samples, they do provide the basis for a discussion of the type of graphite needed for a coating base. Graphites 2, 4 and 5 have a higher radiation-induced contraction rate than is desirable for reactor use. Graphite 6 was damaged and could not be measured. Graphites 1 and 3 appear fairly stable. The effect of irradiation evidenced here could contribute to the apparently high incidence of coating failure on graphites 2, 4, 5 and 6 as compared with coatings on graphites 1 and 3.

Data in Table IV indicate another probable cause for cracking and subsequent failure. Graphite 3, on which coatings had an excellent survival factor, is quite isotropic as evidenced by the ratio of the coefficients of thermal expansion (CTE) in the $\perp$ / $\parallel$ direction.* Graphites 5 and 6 with a higher incidence of coating failure, are less isotropic. The thermal expansion characteristics of isotropic graphites more closely match those of SiC; therefore, the coating would be stressed less during high-temperature irradiation. Since the orientation of graphite samples 1, 2 and 4 is not known, this comparison cannot be reasonably extended.

* $\perp$ and $\parallel$ refer respectively to samples taken transverse and parallel to the extrusion axis of the bar.

TABLE IVTHERMAL EXPANSION COEFFICIENTS OF COATING BASE GRAPHITES

<u>Graphite</u>	<u>Orientation</u>	<u>CTE x 10⁶ ($\frac{\text{in}}{\text{in } ^\circ\text{C}}$)</u> <u>25 C - 425 C</u>	<u>Ratio</u> <u>CTE $\frac{\perp}{\parallel}$</u>
1	Unknown	6.53	
2	Unknown	4.30	
3	Parallel	3.87	1.28
3	Transverse	4.97	
4	Unknown	4.39	
5	Parallel	2.34*	1.48
5	Transverse	3.64	
6	Parallel	2.22*	1.70
6	Transverse	3.58	
Silicon Carbide		4.0	

*Estimated from a different temperature range

CONCLUSIONS

There was no visual evidence of radiation damage to the SiC. All coating failures apparently resulted from stresses in the coating, originating from either radiation or thermally induced dimensional changes in the graphite. Although the number of samples is limited, there is significant evidence, to indicate that SiC-coated graphites can be used successfully in reactor applications if the base graphite is carefully selected. For example, coatings on graphite 3, with a $\perp/\parallel$ -CTE ratio of 1.28 and good radiation stability, showed relatively little cracking or other damage during irradiation.

FIGURE 1
Polished Section of SiC Coating on Graphite
(Side View of Cylinder, 100 X)

SiC Coating

Base Graphite

Graphite Pore

FIGURE 2

Polished Section of SiC Coating on Graphite
(Corner View of Cylinder, 100 X)

FIGURE 3

Polished Section of SiC Coating on Graphite
(End View of Cylinder, 100 X)

FIGURE 4
Polished Section of Cracked-Oxidized SiC. Coating on Graphite
(1/2 Section of Cylinder, 6-1/2 X)

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