THE WDC-I-I INSTRUMENTED
IRRADIATION OF BORON CARBIDE
IN A SPECTRUM-HARDENED ETR FLUX

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April 1973

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by

A. L. Pitner

ABSTRACT

Boron carbide pellets were irradiated in a spectrum-hardened ETR flux at temperatures of 1220 to 1620°F up to maximum specimen-averaged exposures of 38×10^{20} captures/cc. Material variables included pellet density (75 to 99% T.D.) and stoichiometry (B:C = 3.8 to 4.1). Gas release and irradiation temperature were continuously monitored during the irradiation. Results are reported for boron carbide structural degradation, helium release, and interaction with Type 316 stainless steel.

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THE WDC-1-1 INSTRUMENTED IRRADIATION OF BORON CARBIDE IN A SPECTRUM-HARDENED ETR FLUX

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INTRODUCTION

Boron carbide has been selected as the absorber material for the Fast Flux Test Facility (FFTF) and is a leading control material candidate for future Liquid Metal Fast Breeder Reactors (LMFBR's). From a neutronics standpoint, boron carbide is an attractive absorber since the neutron capture cross section of ^{10}B is one of the largest of all known isotopes in a fast reactor flux. A possible disadvantage of boron carbide, however, is that it evolves gas during irradiation. Neutron absorption is accomplished by the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction, thus helium gas is generated during the irradiation of boron carbide. Some of the helium is released from the boron carbide, and the associated gas pressure buildup in the control pin plenum can ultimately limit control rod lifetimes. LMFBR control element design consequently requires a knowledge of gas release behavior as a function of burnup and irradiation temperature. A primary objective of the WDC-1-1 experiment was to obtain this type of information by continuous monitoring of sample gas pressures and temperatures during irradiation. The experiment was conducted in the Engineering Test Reactor (ETR) because of the relative ease of instrumenting experiments in this facility.

Although there has been considerable irradiation testing of boron carbide in thermal reactors,⁽¹⁻⁴⁾ little data have been generated on its irradiation performance in fast reactor spectra. Because the absorption cross section of ^{10}B in a thermal reactor spectrum is very large (~ 4000 barns), there is considerable self-shielding and most reactions are localized near the surface of the absorber pellet. The cross section in a fast reactor spectrum, however, is much smaller (~ 1 barn), and reactions occur uniformly through the material. Also, the ratio of (n,n) scattering reactions to (n,α) absorption reactions is different in the two spectra. Consequently, the irradiation performance of boron carbide in various reactor spectra might easily be expected to differ. Since the ETR is also basically a thermal reactor, it was necessary to employ

neutron filters in this experiment to tailor the flux to a shape more representative of LMFBR-type spectra. This experiment was a follow-on to a similar test irradiated previously in the ETR,⁽⁵⁾ and was constructed with the same basic design.

The experiment test matrix is summarized in Table I. The base material was patterned after the reference boron carbide for the FFTF and was selected as hot-pressed pellets of 90% T.D. with a B:C ratio of 4.0. Sample densities were varied from 75% T.D. to 99% T.D. and stoichiometries from $B_{3.8}C$ to $B_{4.1}C$. These ranges represented commercial fabrication capabilities at the time and were chosen to provide performance data on boron carbide with material parameters bracketing those of the FFTF reference boron carbide. Twelve of the samples were hot-pressed, while the remaining two were cold-pressed and sintered. Irradiation parameters were selected to be representative of FFTF and LMFBR conditions. Irradiation temperatures ranged from 1220 to 1620°F, while sample volume-averaged burnups ranged from 14 to 38×10^{20} captures/cc. Since there are $\sim 10^{23}$ boron atoms/cc in boron carbide, the maximum exposure here represents $\sim 4\%$ burnup of the boron.

TABLE I
EXPERIMENT TEST MATRIX

Pellet Density	75, 90, 93, 96, and 99% T.D.
Stoichiometry	B:C = 3.8, 4.0, and 4.1
Fabrication	Hot-Pressed and Cold-Pressed/Sintered
Temperature	1220 to 1620°F
Burnup	14 to 38×10^{20} captures/cc

EXPERIMENTAL

A typical section of the WDC-1-1 capsule is shown schematically in Figure 1. Each of the fourteen specimens was comprised of three boron carbide pellets nominally 0.25-in. diameter x 0.25-in. long. Enriched (92% ^{10}B) boron carbide was utilized to enhance reaction rates. A Type 316 stainless steel wafer was positioned on top of several of the samples to investigate interaction between the materials during irradiation. The samples were contained in sealed Type 304 stainless steel sample holders. A stainless steel sheathed chromel-alumel thermocouple measured the irradiation temperature of each sample, and a capillary gas tube connected each sample to an external pressure-

FIGURE 1. Schematic of Irradiation Capsule.

measuring transducer. The sample train was contained in a 1.5-in. diameter stainless steel tube. Temperatures were controlled by varying the composition (hence, thermal conductivity) of the helium/argon binary gas that purged the capsule between the sample holders and containment tube. The gas was purified by heated copper turnings and dessicant prior to entering the capsule to minimize oxidation of capsule components. Temperature control was maintained on samples near the center of the capsule. Due to the upward shift of flux as control rods were withdrawn to compensate for fuel burnup in the ETR, sample temperatures at the extremities of the capsules varied $\sim 150^{\circ}\text{F}$ from beginning to end of each cycle. Sample temperatures near the center of the capsule varied less than 50°F .

Irradiation of boron carbide in an unperturbed ETR flux would result in reaction gradients of $\sim 100:1$ from surface to center of the pellets due to self-shielding effects. To modify the spectrum to obtain reaction profiles more representative of LMFBR conditions, neutron filters of cadmium and boral (35 wt% B_4C - 65 wt% aluminum) were employed in the experiment. The 0.150-in. thick cadmium shroud that surrounded the capsule (Figure 1) eliminated the thermal flux, while the 0.150-in. thick boral liner located inside the containment tube reduced the epithermal component of the flux. Calculations were performed with the DTF transport theory code,⁽⁶⁾ and details are given in Reference 5. Figure 2 shows the calculated spectrum at the surface of the boron carbide. The unperturbed ETR spectrum and Fast Test Reactor (FTR) spectrum are also included for comparison. The neutron filters were effective in removing the lower-energy component of the flux such that a fast reactor spectrum was approximated. The calculated reaction gradient through the sample is shown in Figure 3. There are approximately four times as many reactions at the surface of the pellet than in the center. As indicated previously, the reaction gradient in an unperturbed ETR flux would be $\sim 100:1$ from surface to center; while in an LMFBR spectrum, there would be essentially no gradient at all. The reaction gradient in the WDC-1-1 experiment could have been reduced further by additional filtering, but space constraints precluded this. Calculations showed that the filters used were of adequate thickness to avoid significant burnout effects. The calculated reaction profile at the end of the irradiation varied negligibly from that at the beginning. Additional filtering would also have reduced overall reaction rates and required longer irradiation times to obtain goal burnups in the samples. The neutron filters used, coupled

FIGURE 2. Calculated Spectra Showing Effect of Neutron Filters.

FIGURE 3. Reaction Gradient Through B_4C Sample.

with detailed physics analyses and dosimetry, thus provided a spectrum which approximated that of a fast reactor and was known so that irradiation effects could be evaluated.

Physics calculations to predict reaction rates and flux gradients in the experiment were performed on a relative basis and required normalization to obtain quantitative values. In order to measure the incident thermal flux magnitude and obtain this normalization factor, four Self-Powered Neutron Detectors (SPND's)⁽⁷⁾ were located outside the cadmium shroud tube. Each SPND consisted of a central vanadium "emitter" wire separated from an Inconel "collector" sheath by Al_2O_3 insulation. Each thermal neutron capture in the vanadium results in ejection of a beta particle (electron) that is collected on the sheath. An electric current is thus induced between the emitter and sheath that is proportional to the thermal flux. Measurement of this current

(via measurement of the voltage drop across an external resistor connected to the SPND by coaxial cable) then gives a measure of the thermal flux. Sensitivity of the vanadium SPND's was 1.5×10^{-21} amp/nv, so measurement of ~ 4 mv voltage drop across a 20,000 ohm restrictor indicated a thermal flux of $\sim 1.3 \times 10^{14}$ nv, which was within the predicted range. The four 8-in. long SPND's were positioned atop one another to give an indication of the axial flux profile through the capsule.

Continuous data recording was accomplished with the use of multipoint chart recorders. Figure 4 is a photograph of the instrumentation consoles for the experiment. The console on the left contains the flux recorder and pressure transducers and bleed valves (for venting helium when pressures approached transducer limits). A pressure gauge connected to a common manifold with the transducers was used to calibrate the transducers periodically. The central console contains the temperature recorder and gas flow controls. The gas purification systems are at the back of the panel. The high temperature alarm (buzzer) on the panel signaled when temperatures were 25°F above normal. Sounding of this alarm required an increase in helium flow to cool capsule temperatures. A time meter that was activated only during irradiation (tripped when specimen temperatures reached operating levels) kept a running record of elapsed irradiation time. The panel at the right monitored the pressure transducer outputs. Data were also taken from the recorders and entered on a separate log sheet once per shift. This provided a convenient tabular record of irradiation data, while detailed results remained available on the recorder charts if such reference were necessary. The irradiation lasted four reactor cycles, or approximately 4400 hours. Four of the fourteen pressure monitoring systems developed leaks during this time, two of them near the end of the irradiation. Only one of the fourteen thermocouples failed during the test, that one after two cycles of irradiation.

SAMPLE CHARACTERIZATION

All samples were fabricated from boron carbide powder enriched to $\sim 92\%$ ^{10}B . Vendor-supplied analyses of the powder are given in Table II. The B:C ratio of the powder was 4.08; total impurities were less than 0.5 wt%. The hot-pressed pellets were fabricated at HEDL. Elemental boron (enriched) and carbon were added to alter stoichiometry as required by the test matrix. The cold-pressed and sintered pellets were fabricated by a commercial vendor from

FIGURE 4. Instrumentation and Control Consoles.

the same powder. In order to obtain the required pellet density, powder for the sintered pellets was ground to obtain finer material. This grinding operation (tungsten carbide ball-milling) unfortunately introduced impurities into the material.

TABLE II
BORON CARBIDE POWDER ANALYSES

CHEMISTRY:	Constituent	wt%
	Boron	76.8
	Carbon	22.4
	B ₂ O ₃	< 0.2
	Fe + Cr + Ni	0.052
	Al	ND
	Ca	0.0023
	Other	0.02
ENRICHMENT:	¹⁰ B in Boron	91.7 atom%
PARTICLE SIZE:	Microns	wt%
	-104	99.9
	-74	99.9
	-44	96.8
	-20	43.8
	-10	22.8

Characterization data of all sample types are summarized in Table III. Densities are based on a theoretical value of 2.38 g/cc for 92% ¹⁰B enriched boron carbide. B:C ratios are based on total boron and total carbon analyses. Grain sizes were determined by the random intercept method (uncorrected). Grain size for all the hot-pressed material ranged from 9 to 14 microns, with the exception of the 96% T.D. pellets which were 18 microns. The cold-pressed and sintered pellets were very fine-grained, less than 3 microns. Considerable impurity was present in this material, as shown in the table.

Figures 5, 6, and 7 are micrographs of the 75, 90, and 99% T.D. material, respectively. Structure is similar among the materials except for different degrees of porosity corresponding to the relative pellet densities. Pellets of 93 and 96% T.D. showed correspondingly decreasing levels of porosity between that of the 90 and 99% T.D. materials. Figure 8 is a micrograph of a cold-pressed and sintered sample. This material is 83% T.D. The finer texture of this material is readily evident by comparison with the hot-pressed samples. The large dark areas in Figure 8 are graphite concentrations. The higher free carbon content in the sintered material is also reflected in the chemical

TABLE III
SAMPLE CHARACTERIZATION DATA

Sample ID	% T.D.	B:C Ratio	Average Grain Size (μm)	Free B (wt.%)	Free C (wt.%)	Total Impurities (wt.%)
75% T.D.	75	4.0	10	0.2	0.7	< 0.5
90% T.D.	90	4.0	9	0.2	0.6	< 0.5
93% T.D.	93	4.0	14	0.2	0.7	< 0.5
96% T.D.	96	4.0	18	0.2	0.7	< 0.5
99% T.D.	99	4.0	14	0.2	0.7	< 0.5
B:C = 3.8	90	3.8	11	0.0	1.8	< 0.5
B:C = 4.1	90	4.1	14	0.2	0.5	< 0.5
Sintered	83	3.9	< 3	1.3	2.0	11.0*

*4% W, 5% Si, 1% Ni, 0.5% Fe.

FIGURE 5. Microstructure of 75% T.D. Pellet (250X magnification).

FIGURE 6. Microstructure of 90% T.D. Pellet (250X magnification).

FIGURE 7. Microstructure of 99% T.D. Pellet (250X magnification).

FIGURE 8. Microstructure of Cold-Pressed and Sintered Pellet (250X magnification).

FIGURE 9. Electron Microprobe Trace of Cold-Pressed and Sintered Pellet Showing Metallic Inclusions (1000X magnification).

analyses in Table III. Figure 9 is an electron microprobe trace of back-scattered electrons that depict metallic inclusions as white spots in the sintered material. These inclusions were identified as being primarily tungsten in additional microprobe work.

RESULTS AND DISCUSSION

FLUX CHARACTERIZATION

Proper evaluation of irradiation effects required characterization of the neutron flux incident on the boron carbide samples. To define the spectral shape and intensity of the neutron flux, a set of six flux monitors were located near the center of the capsule. Table IV lists the neutron reactions used in the spectral analysis. The energy response ranges over which 90% of the reactions occur are also given in the table. The normalized flux spectrum derived from the dosimetry analysis is shown in Figure 10, along with the previously calculated spectrum.⁽⁵⁾ In general, the measured spectrum agrees well with the calculated spectrum, thereby confirming the neutronic design basis for the experiment. Average energy of the calculated spectrum is 0.89 MeV, while that of the measured spectrum is 0.74 MeV.

TABLE IV
DOSIMETRY MONITOR REACTIONS AND RESPONSE RANGES

Reaction	90% Response Ranges, MeV	
	E_{Lower}	E_{Upper}
${}^4_6\text{Ti}(n,p){}^4_7\text{Sc}$	3.4	9.5
${}^{58}_{28}\text{Ni}(n,p){}^{58}_{27}\text{Co}$	1.9	7.9
${}^{54}_{26}\text{Fe}(n,p){}^{54}_{25}\text{Mn}$	1.9	7.5
${}^{237}_{93}\text{Np}(n,f)$	0.525	4.2
${}^{59}_{27}\text{Co}(n,\gamma){}^{60}_{27}\text{Co}$	1.35×10^{-5}	3.4×10^{-4}
${}^{45}_{21}\text{Sc}(n,\gamma){}^{46}_{21}\text{Sc}$	8.8×10^{-7}	1.43×10^{-1}

The derived total flux at the center of the capsule was 7.7×10^{14} n/cm²-sec. Total fluence was 1.15×10^{22} n/cm². The calculated burnup of the boron carbide sample located nearest the dosimetry set, based on the measured flux shape and intensity, was 35.4×10^{20} captures/cc. This agrees well with the measured burnup for this sample, 38.0×10^{20} captures/cc.

To verify that the neutron filters used in the experiment were effective

FIGURE 10. Normalized Flux Incident on Boron Carbide Samples.

in eliminating the thermal flux component throughout the capsule, bare and gadolinium-covered flux monitors of cobalt, scandium, iron, and tantalum were positioned near the center and at both ends of the capsule. If thermal neutron leakage had occurred, there would have been significant differences in the activities of the bare and covered monitors, since the gadolinium would have absorbed the thermal neutrons before they could activate the enclosed monitors. Within experimental error, no difference in the activities of bare and gadolinium-covered monitors was noted. This verified that the filters performed properly for the full duration of the test and no significant leakage of thermal neutrons occurred.

BURNUP

The axial burnup profile through the experiment was determined by activation analysis of iron gradient wires positioned throughout the capsule. This correlation is justified since the reaction that generates the ^{59}Fe isotope in iron has similar energy response to that for the (n,α) reaction in ^{10}B in a fast spectrum. The iron activation results, however, defined only the shape of the burnup profile, and an absolute burnup analysis was required to pin the burnup profile curve at some point. This was accomplished by vacuum-annealing an entire sample (No. 6) and measuring the total volume of helium that had been retained in the material. This quantity in conjunction with the evolved quantity measured during irradiation then defined the total amount of helium generated, and hence the burnup of that sample. The results are shown in Figure 11. Portions of two other samples (Nos. 1 and 10) were vacuum-annealed to provide a check on the above analysis. Reasonably good agreement was obtained, as seen in the figure. In general, sample burnups were within $\sim 20\%$ of estimated values based on calculated reaction rates.

Burnups determined by the above method are sample volume-averaged values. Unless otherwise stated, the burnups cited throughout this report refer to volume-averaged values. However, it should be remembered that, because of the reaction gradients through the samples, burnups near the surface are significantly greater than the volume-averaged values. Burnup on the outer surface is actually approximately four times as great as the sample average burnup. Approximately 20% of the total reactions occur in the outer 10% shell volume of each pellet where the effective burnup is approximately twice as great as the average value. Consequently, overall sample behavior can be

FIGURE 11. Burnup Profile Through the Capsule.

significantly affected by what transpires in the outer high-burnup region. Observed structural changes, in particular, can be related to this gradient effect.

PELLET STRUCTURE

The boron carbide pellets in general were quite friable after the irradiation. The degree of pellet breakup appeared to be a function of position (and consequently exposure) in the capsule. Figure 12 shows the No. 1 sample (located at top of capsule where flux was lowest) that was irradiated to 14×10^{20} captures/cc at 1260°F. The short (1/8-in. long) pellet was included as a metallographic specimen. These pellets survived the irradiation well and are completely intact. Figure 13 shows a sample irradiated at an intermediate flux position (No. 5) to 28×10^{20} captures/cc at 1580°F. Although the pellets for the most part are whole, some degradation at the corners is evident. Sample No. 10 irradiated in the maximum flux position to 38×10^{20} captures/cc at 1580°F is shown in Figure 14. Pellet breakup here is quite severe.

Although a 0.040-in. diametral gap was allowed between the 0.250-in.

FIGURE 12. Pellets Irradiated at 1260°F to 14×10^{20} Captures/cc.

FIGURE 13. Pellets Irradiated at 1580°F to 28×10^{20} Captures/cc.

FIGURE 14. Pellets Irradiated at 1580°F to 38×10^{20} Captures/cc.

diameter pellets and their holders to accommodate swelling, several of the samples were stuck in their holders after irradiation. Specifically, samples No. 3, 6, 8, 9, 10, and 11 had to be forced out of their holders. Although this forcing operation was responsible for much of the pellet fracturing, several of the pellets that were removed easily in one piece crumbled when subsequently disturbed. Only about half of the irradiated pellets were recovered intact.

Figure 15 shows the end view of a 93% T.D. pellet that was irradiated to 25×10^{20} captures/cc at 1460°F. Another pellet rested on this surface and consequently served to shield it from the flux. The periphery of the pellet has a visibly different appearance than the central portion. This surface effect was noted to a larger degree in thermal reactor irradiations,⁽⁴⁾ and is attributed to the reaction gradient through the sample (see Figure 3). This effect is not expected in a fast reactor flux. Circumferential cracking can be seen just inside the high burnup region, and some radial cracking is also present. Figure 16a shows the end of a 90% T.D. pellet irradiated to 28×10^{20} captures/cc at 1580°F. This end was also shielded from the flux by another pellet. Again the peripheral region has a different appearance, and there is severe radial cracking present. The cracks probably develop as a result of differential stresses set up between the surface and core regions due to differential irradiation-induced volume swelling associated with the

FIGURE 15. 93% T.D. Pellet Irradiated at 1460°F to 25×10^{20} captures/cc.

FIGURE 16a. 90% T.D. Pellet Irradiated at 1580°F to 28×10^{20} Captures/cc.

FIGURE 16b. Side View of Pellet in Figure 16a.

reaction gradient through the sample. This differential swelling is further dramatized in Figure 16b, which shows a side view of the same pellet shown in Figure 16a. The bottom face of the pellet was exposed to the flux while the top surface was shielded by another pellet. There is a noticeable flaring of the pellet at the bottom end that can be correlated with the increased exposure (hence increased volume swelling) this open end received. The calculated reaction gradient through the sample ($\sim 4:1$) would indicate that the exposed surface of this pellet received an exposure of $\sim 100 \times 10^{20}$ captures/cc, or $\sim 10\%$ boron burnup.

Figure 17 is a micrograph of a 96% T.D. pellet irradiated to 22×10^{20} captures/cc average burnup at 1320°F . Considerable grain boundary cracking can be seen near the surface region, while the interior of the pellet has an essentially undisrupted appearance. In general, this same effect was seen in all irradiated pellets examined ceramographically: considerable degradation

FIGURE 17. Micrograph of 96% T.D. Pellet Irradiated at 1320°F to 22×10^{20} Captures/cc.

near the surface where burnup was greatest, and little change in interior microstructure from that of the unirradiated material, with the exception of a few large cracks that traversed the interior of some of the samples. Material pullout near pellet surfaces during polishing for ceramographic examination was common due to loss of structural integrity in this high-burnup region. In general, it appears that significant physical degradation occurs when local burnup exceeds $\sim 50 \times 10^{20}$ captures/cc.

GAS RELEASE

Gas release behavior of each of the fourteen samples is shown as a function of burnup in Figures 18 through 31. The solid curve in each figure represents measured gas release in units of cubic centimeters at standard temperature and pressure conditions. The dashed line represents fractional gas release based on the burnup analysis. The release fraction at any point refers to what portion of the total gas generated to that point has been released, not the instantaneous release rate. Final exposure and temperature history are also shown on each of the figures. As indicated previously, samples near the capsule ends (e.g., Nos. 1, 2, 13, and 14) experienced rather large temperature swings from beginning to end of each reactor cycle. Gas pressure-monitoring systems on several of the samples (Nos. 2, 8, 9, and 12) developed leaks before the irradiation was completed. Sample No. 6 had a small leak during the early portion of the irradiation that was subsequently repaired. This accounts for the apparent discrepancy between samples No. 5 and 6. The system on sample No. 3 was apparently plugged (no pressure changes) during much of the interim irradiation, but opened up near the end of the test. One thermocouple (No. 6) failed approximately halfway through the irradiation.

The general gas release behavior of the samples was to show increasing gas release during the early portion of the irradiation followed by a decrease in release rate. Gas release then continued at essentially a constant rate up to $\sim 25 \times 10^{20}$ captures/cc, whereafter gas release at the higher temperatures (1550 to 1600°F) began to increase again slightly. For samples irradiated at 1550 to 1600°F (with the exception of the 75% T.D. material), the integrated release fraction reached a maximum of 25 to 35% at a burnup generally less than 5×10^{20} captures/cc and then began to decrease. Samples irradiated at 1250 to 1500°F generally had maximum integrated release fractions of 55 to 70%, and did not begin decreasing until the burnup reached 6 to 8×10^{20} captures/cc.

FIGURE 18. Gas Release Behavior of Sample No. 1 (90% T.D.).

FIGURE 19. Gas Release Behavior of Sample No. 2 (99% T.D.).

FIGURE 20. Gas Release Behavior of Sample No. 3 (96% T.D.).

FIGURE 21. Gas Release Behavior of Sample No. 4 (93% T.D.).

FIGURE 22. Gas Release Behavior of Sample No. 5 (B:C = 3.8).

FIGURE 23. Gas Release Behavior of Sample No. 6 (B:C = 3.8).

FIGURE 24. Gas Release Behavior of Sample No. 7 (B:C = 4.1).

FIGURE 25. Gas Release Behavior of Sample No. 8 (93% T.D.).

FIGURE 26. Gas Release Behavior of Sample No. 9 (90% T.D.).

FIGURE 27. Gas Release Behavior of Sample No. 10 (99% T.D.).

FIGURE 28. Gas Release Behavior of Sample No. 11 (95% T.D.).

FIGURE 29. Gas Release Behavior of Sample No. 12 (75% T.D.).

FIGURE 30. Gas Release Behavior of Sample No. 13 (Sintered).

FIGURE 31. Gas Release Behavior of Sample No. 14 (Sintered).

The gas release fractions of the samples at a burnup of 25×10^{20} captures/cc are plotted as a function of irradiation temperature in Figure 32. In cases where sample exposures did not reach 25×10^{20} captures/cc (samples irradiated at $\sim 1250^\circ\text{F}$), the plotted values were obtained by extrapolation of the gas release curves. Several observations can be made of the data in this form. Gas release at this exposure decreases as irradiation temperature increases from 1250°F to $\sim 1600^\circ\text{F}$. At 1250 to 1500°F , the gas release fractions range from 30 to 50%, while at 1550 to 1600°F they are only 10 to 20%, with the exception of that of the low density (75% T.D.) material which is 25%. It should be remembered, however, that the low temperature ($\sim 1250^\circ\text{F}$) data points were obtained by extrapolation of existing data and consequently are somewhat uncertain. Also, gas release fractions are beginning to increase with additional exposure at 1600°F , while they are still decreasing with exposure at 1250°F . This trend of course would make the above temperature correlation less pronounced at higher exposures.

The effect of pellet density on gas release can be compared at a temperature of $\sim 1600^\circ\text{F}$. Gas release decreases as pellet density increases, particularly from 75% T.D. to 93% T.D. The effect of density on gas release in the 93 to 99% T.D. range, however, is quite small.

It appears that the 96% T.D. sample at 1320°F releases noticeably less gas than a 90% T.D. sample would at this temperature. In addition to the increased density effect, grain size of the 96% T.D. material is twice as large as that of the 90% T.D. pellets (18 versus 9 microns). Since the average diffusion path for helium atoms to grain boundaries in large-grained material is longer, this characteristic could be largely responsible for the decreased gas release behavior observed here.

The effect of stoichiometry on gas release near 1600°F appears to be less gas release in the $\text{B}_{4.1}\text{C}$ material than in the $\text{B}_{3.8}\text{C}$ material (14 versus 19%). However, the larger grain size of $\text{B}_{4.1}\text{C}$ sample over that of the $\text{B}_{3.8}\text{C}$ sample (14 versus 11 microns) may again be partly responsible for the observed behavior.

The cold-pressed and sintered sample irradiated at 1500°F released considerably more gas than the other samples near this temperature. This behavior might well be expected based on the low density (83% T.D.) and fine grain (< 3 microns) characteristics of this material. At 1250°F , the extrapolated gas

FIGURE 32. Fraction Gas Release at 25×10^{20} Captures/cc.

release fraction of this material at 25×10^{20} captures/cc appears to agree with that of the other samples. Again, some uncertainty exists in the data points at this temperature due to extrapolation of the data.

The observed gas release behavior of samples irradiated in this test appears to go through several distinct stages. During the very early portion of the irradiation, gas release increases with exposure. This is not unexpected since some inventory of helium must be built up in the material before significant release occurs. A concentration gradient must be developed to provide a driving force for helium migration. The release rate then approaches a constant value before beginning to decrease with additional exposure. This decrease is believed to be a result of a helium trapping mechanism coming into dominance. The decrease occurs earlier at the higher irradiation temperatures, and thus may be thermally-induced. Gas release undoubtedly is a consequence of several competing mechanisms, and while higher temperatures would promote diffusion of helium atoms out of grains and out of the pellet, the development of trapping sites at the higher temperatures (1550 to 1600°F) evidently is most influential in controlling helium release and causes a net reduction in the release rate. As noted previously, integral gas release fractions begin decreasing at lower burnups and have smaller maximum values at temperatures of 1550 to 1600°F than they do at lower temperatures. The next stage of gas release appears to be relatively constant release at the reduced rate. At the higher temperatures, the gas release rate begins to increase again after the burnup reaches 20 to 25×10^{20} captures/cc and is still increasing slowly at the highest burnup attained in the test ($\sim 35 \times 10^{20}$ captures/cc). The few lower temperature samples that approach a burnup of 25×10^{20} captures/cc do not yet show any indication of increase in release rate. These observations might suggest that the trapping sites are approaching their limit for retaining helium at the higher temperatures. Additional accumulation of helium at these sites may cause stresses to exceed the material strength resulting in localized fracture and release of helium. At the lower temperatures, not nearly as much gas has been retained and the trapping sites have not yet reached their equilibrium density and size. The eventual increase in release rate at the lower temperatures therefore would be expected to be delayed from that at higher temperatures.

The trend of increasing gas release cited above is said to begin at sample-averaged burnup levels of 20 to 25×10^{20} captures/cc for irradiation

temperatures of 1550 to 1600°F. As pointed out earlier, however, the observed increase might actually reflect what is happening in the outer high-burnup regions of the samples. For instance, if gas release were actually 50% in the outer 10% volume of the sample and 10% in the remaining 90% core region, the net gas release fraction would be nearly $\sim 17\%$. This possibility itself could account for much of the observed gas release behavior. Consequently, the apparent slight increase in gas release at $\sim 25 \times 10^{20}$ captures/cc (volume-averaged) may actually represent a much larger increase at higher exposures. In a fast reactor, therefore, gas release may not begin to increase until burnups exceed something greater than 25×10^{20} captures/cc.

Gas release appears to be inversely proportional to pellet density and material grain size. The latter observation implies that grain boundary diffusion plays a significant part in helium release from the material. That is, once a helium atom reaches a grain boundary, the probability for escape is enhanced. In large-grained material the average diffusion path to grain boundaries is longer and helium release is effectively restricted. Reaching a grain boundary, however, apparently does not ensure release of the helium atom. Previous electron microscopic examinations⁽⁸⁾ of irradiated boron carbide by ORNL showed concentrations of helium bubbles along grain boundaries. These, too, can act as trapping sites for individual helium atoms. Growth and coalescence of these bubbles are reported⁽⁸⁾ to cause eventual grain-boundary cracking, which could also increase gas release.

Increased gas release at lower pellet densities is reasonable behavior. Pellets of lower density would be expected to contain a greater degree of open porosity, and once the migrating helium atoms intercept this open porosity they are released from the material. The fact that little difference in behavior between the 93 to 99% T.D. pellets was seen suggests there may be little difference in the open porosity content of these samples; i.e., the variations in density may be attributable to the degree of closed porosity.

B₄C INTERACTION WITH TYPE 316 STAINLESS STEEL

Type 316 stainless steel has been designated as the cladding material for fuel and control material pins in the FFTF. Interaction between Type 316

stainless steel and boron carbide has been well characterized in out-of-reactor compatibility tests.⁽⁹⁾ To investigate whether the interaction might be accelerated under irradiation, wafers of Type 316 stainless steel were positioned on top of several of the boron carbide samples in the WDC-1-1 experiment, as shown in Figure 1. The wafers were examined metallographically after the irradiation. Figure 33 shows a micrograph of a wafer that was irradiated in contact with boron carbide at 1460°F for 4400 hours. The wafer is 0.030-in. thick, and the depth of interaction is ~ 0.009 -in. The wafer in Figure 34 was irradiated at 1580°F. Here the reaction has essentially proceeded through the entire stainless steel specimen. Localized volume swelling associated with the interaction on the side in contact with the boron carbide has actually caused the wafer to bow. In general, the degree of interaction increased with irradiation temperature. Results of all eight specimens examined are summarized in Figure 35. The out-of-reactor compatibility curve is also included as a reference. Nearly all the WDC-1-1 data points lie below the out-of-reactor curve. This might be expected since the wafers in this experiment contacted the boron carbide only with the force of their own weight (~ 0.2 gram), while in the laboratory tests large hydrostatic pressures (≥ 3000 psi) were used to insure good physical contact between the materials. The results observed here would indicate that interaction between Type 316 stainless steel and boron carbide is not aggravated under irradiation. Since FFTF and LMFBR cladding temperatures are in the range where interaction rates are low ($\sim 1100^\circ\text{F}$ or less), loss of cladding integrity due to interaction with boron carbide would not appear to be a problem even if gap closure were to occur.

SUMMARY AND CONCLUSIONS

The WDC-1-1 instrumented experiment containing boron carbide samples was irradiated in a spectrum-hardened ETR flux for 4400 hours. Neutron filters of cadmium and boral were effective in reducing the reaction gradient through the 0.25-in. diameter samples to a ratio of $\sim 4:1$ from pellet surface to center-line. By comparison, the ratio would be $\sim 100:1$ in an unperturbed ETR flux, while in an LMFBR spectrum there would be almost no gradient at all. Dosimetry analyses verified that the filter components performed properly throughout the irradiation.

FIGURE 33. Type 316 Stainless Steel
Irradiated in Contact with
Boron Carbide at 1460°F
for 4400 Hours.

FIGURE 34. Type 316 Stainless Steel
Irradiated in Contact with
Boron Carbide at 1580°F
for 4400 Hours.

FIGURE 35. Summary of B₄C-Type 316 Stainless Steel Interaction Data from WDC-1-1 Irradiation.

Sample temperatures and gas release were continuously monitored during the irradiation. Temperatures ranged from 1220 to 1620°F, while sample-averaged burnups ranged from 14 to 38×10^{20} captures/cc. The maximum burnup corresponds to $\sim 4\%$ depletion of the total boron atoms. Material variables investigated were pellet density (75 to 99% T.D.) and stoichiometry (B:C = 3.8 to 4.1). Twelve of the fourteen irradiation samples were hot-pressed, while two were cold-pressed and sintered.

The boron carbide samples in general were very friable after irradiation. Surface regions were noticeably more deteriorated than pellet interiors due to the higher exposure the surface regions received as a result of reaction gradients through the samples. It appears that physical degradation becomes pronounced when local burnups exceed $\sim 50 \times 10^{20}$ captures/cc. About half of the irradiated samples had to be forced from their holders due to volume expansion, even though a 0.040-in. diametral clearance had been allowed to accommodate swelling of the 0.25-in. diameter pellets.

Gas release was found to be highly dependent on irradiation temperature and burnup. The release rate in all samples decreased after some initial exposure. Samples irradiated at 1250 and 1550°F generally began showing a decrease in gas release after a maximum integrated release fraction of 55 to 70% was reached at burnup of 6 to 8×10^{20} captures/cc. Gas release of samples irradiated at 1550 to 1600°F, on the other hand, generally began decreasing before 5×10^{20} captures/cc after showing maximum integrated release fractions of only 25 to 35%. Gas release continued at the reduced rate up to exposures of $\sim 25 \times 10^{20}$ captures/cc, where release in the higher temperature samples (1550 to 1600°F) began increasing again slightly. It is speculated that the observed increase in gas release may actually be due to higher release rates in the outer high-burnup regions of the samples, and would not be observed in a fast reactor flux until burnups exceeded 25×10^{20} captures/cc. No subsequent increase in gas release in the 1250 to 1500°F samples was noted up to the highest exposure attained at these temperatures ($\sim 25 \times 10^{20}$ captures/cc). At 25×10^{20} captures/cc, fractional gas release for samples irradiated at 1250 to 1500°F were generally 30 to 50%, while at 1550 to 1600°F only 10 to 20% of the helium generated had been released. The observed gas release behavior suggests the development of a helium-trapping mechanism with irradiation exposure. The

mechanism is apparently thermally-dependent since gas release in the 1550 to 1600°F samples is less and begins decreasing sooner than samples irradiated at 1250 to 1500°F. In regard to the effects of material properties on gas release, 75 and 83% T.D. pellets showed significantly more gas release than 90 to 99% T.D. pellets. Little effect of pellet density on gas release in the 90 to 99% T.D. range was noted. Pellets with a B:C ratio of 4.1 seemed to release slightly less helium than those with a B:C = 3.8 to 4.0. Gas release also appeared to vary inversely with material grain size. The cold-pressed and sintered material generally released more gas than the hot-pressed samples. However, the low-density and fine-grain characteristics of the sintered samples were believed to be largely responsible for the observed behavior, and the effect of cold-pressing as a processing variable could not be directly evaluated.

Metallographic examination of Type 316 stainless steel wafers irradiated in contact with boron carbide showed increasing degrees of interaction with increasing irradiation temperature. The results were in generally good agreement with out-of-reactor compatibility data, indicating that interaction between the materials is not aggravated by irradiation.

ACKNOWLEDGEMENTS

Capsule design and assembly was accomplished primarily through the efforts of W. E. Hart. The boron carbide pellets irradiated in the experiment were fabricated and characterized by W. A. Ross and G. L. Jones. Neutronic calculations and spectral analyses were performed by E. P. Lippincott and J. A. Ulseth. J. D. Berger coordinated irradiation activities at the ETR. The contributions of these individuals were vital to the success of this experiment. Appreciation is also expressed to R. E. Dahl and D. E. Mahagin for their comments and suggestions in the writing of this report.

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