NEUTRON IRRADIATION DAMAGE IN BORON CARBIDE

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This paper was prepared for presentation at the Third International Conference on Small Angle X-ray and Neutron Scattering, September 5-8, 1973, at Grenoble, France

The work described in this paper was performed at Pacific Northwest Laboratory, operated by Battelle Memorial Institute for the United States Atomic Energy Commission under contract AT (45-1)-1830, and at Hanford Engineering Development Laboratory operated by Westinghouse Hanford Company under contract AT (45-1)-2170.
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INTRODUCTION

One of the materials being considered for neutron absorbers in Fast Breeder Reactor control systems is boron carbide. The conditions of high flux and high temperature in the new reactor systems produce rather stringent requirements for materials selection. Therefore, characterization of their behavior under irradiation conditions is necessary. The work described in this paper is part of an experimental evaluation of irradiation damage in selected candidate absorber materials.

The high cross section of the reaction, $^{10}\text{B}(n,\alpha)^7\text{Li}$, provides a convenient means for reactor control. As the $^{10}\text{B}$ is depleted with exposure, however, the solid is required to accommodate the lithium and helium reaction products either in solution within the lattice or as precipitates. In addition, the passage of high energy neutrons produces extensive displacement damage, which in most cases results in extensive microstructural alteration.\(^{(1,2)}\)

Evaluation of the irradiation-induced damage state is commonly accomplished with a variety of techniques, each of which complements the others. This paper describes observations and correlations that have been obtained using both transmission electron microscopy (TEM) and small angle x-ray scattering (SAS) to characterize the structure of boron carbide.
EXPERIMENTAL PROCEDURE

The boron carbide used in these studies was obtained from hot-pressed pellets. The samples differed in density by a few percent from the theoretical value, and consisted of well formed grains (average diameter 10-20 microns) with the principal porosity occurring intergranularly. Chemical composition corresponded to B/C ratios of 4.0 ± 0.1.

Irradiation was performed in EBR-II reactor. Irradiation conditions ranged from $6 \times 10^{20}$ captures/cm$^3$ to $17 \times 10^{20}$ captures/cm$^3$ at 500 and 750°C. The irradiated pellets were sectioned, and the section thinned by abrasive grinding to about 1 mm for x-ray scattering measurements. The low x-ray absorption coefficient ($\mu_1 \sim 7.5$ cm$^{-1}$ for Cu K$_\alpha$) dictated the use of these rather thick samples which, fortunately, could be readily prepared.

Small angle scattering experiments were performed with an AMR-Philips small angle goniometer. This instrument utilizes the multiple diffracting collimator system described by Bonse and Hart.(3) With a AMR-Philips point-focus generator, an intense (20,000 counts/sec) primary beam with an angular width of 25 - 30 seconds of angle can be obtained. This collimation system is equivalent to infinitely high, infinitely narrow slits.

Data collection is fully automated. In the work described here, counting time was 100 seconds and counts were repeated at intervals of 10" of angle at low angles (1' - 10'). At higher angles, the interval was usually increased to 30" or 60" of angle.

Electron microscope results presented here were obtained with a 1 MeV JEOL microscope. The B$_4$C samples were thinned by machine lapping to 0.05 - 0.07 mm, followed by ion milling to 5,000 - 10,000 Å for transmission microscopy. Precise sample thicknesses of the areas examined have not yet been determined but thickness variations are apparent.
RESULTS AND DISCUSSION

Small angle scattering results for a $\text{B}_4\text{C}$ specimen irradiated to $17 \times 10^{20}$ captures/cm$^3$ at 500°C are shown in Figure 1. Shown are the direct beam, the scattering from the as-irradiated sample, and the scattering from the sample after annealing 3.5 hours at 1800°C. In Figure 2 the same data are presented after correction for background, as $\ln I$ vs. $\frac{h^2}{2}$ ($h = \frac{4\pi \sin \theta}{\lambda}$). The upper curve (1800°C anneal) has been normalized to $I(0) = 1$ by extrapolation, using the Guinier approximation.\(^{(4)}\)

The scattering for the as-irradiated sample is quite intense, increases sharply with decreasing angle, and cannot be fitted to Guinier's Law. The upward concavity of the $\ln I$ vs. $h^2$ plot at low angles is completely inexplicable by a particle scattering mechanism. An alternative source of scattering is the double-Bragg scattering commonly encountered in deformed materials;\(^{(5)}\) the scattering observed from the as-irradiated sample is assumed to be from this source. The magnitude of this scattering indicates that severe strains exist in the irradiated structure. This conclusion is supported by x-ray diffractometry, which is characterized by severe peak broadening and by the characteristic defect structure shown in Figure 3. This transmission electron micrograph indicates that fast reactor exposure results in the formation of minute platelike pores similar to microcracks in the solid and that extremely strong strain fields are associated with the pores. It is believed that the pores are actually helium bubbles in which the internal pressure is considerably in excess of that required for equilibrium with the solid. This view is shared by others\(^{(6)}\) and is supported by Speight's\(^{(7)}\) analysis for the special case where gas concentrations in a solid are high and the gas diffusivity is much greater than the vacancy diffusion coefficient. Because of these conditions in the as-irradiated material no further attempt was made to interpret the scattering from it.
Annealing causes considerable change in the size and morphology of the bubbles. Small-angle scattering from the sample annealed 3.5 hours at 1800°C after irradiation is characteristic of particle size scattering. The scattering is recorded only at very small angles (1′ - 30′), indicating very large particles. Parallel observations of the microstructure indicated the pore diameters were increased and the intensity of their strain fields was reduced. This is indicative of vacancy flow to the bubbles in order to reduce their pressure to a value which can be maintained in equilibrium with the solid surface tension. Restoration of the x-ray diffraction patterns to a quality comparable to that of the unirradiated material also implies a reduction of lattice strain.

The first conclusion in the interpretation of the scattering was that the expected porosity was present, and that the pores were responsible for the scattering. Additional scattering measurements were made with the sample slab rotated so as to vary the effective thickness; the same curve was obtained in every case. Multiple scattering effects were therefore concluded to be minimal.

The Gaussian portion of the curve extends from 1′ to 3′, and the region of \(1/h^3\) dependence begins at approximately 7′. The pores may therefore be approximated by spheres, as rods or discs would necessitate \(1/h\) or \(1/h^2\) dependence over part of the curve.

The Guinier approximation at the small angles leads to a radium of gyration of 670 Å, corresponding to spheres 1700 Å in diameter. The deviation from the Guinier approximation at increasing angles can only be ascribed to a non-uniform size distribution if the pores are spherical.

The technique employed to determine the size distribution was modified from that proposed by Roess and Shull. This method compares the observed scattering with that calculated for a number of assumed size distributions to determine which combination of parameters yields the best fit. In the present work, a computer was employed to calculate...
the scattering curves for various size distributions. This computer program permitted distribution functions to be changed at will. A correction for slit smearing was included in the program, so the experimental and observed scattering could be directly intercompared. Very briefly, the program evaluated the integral

\[ I(h) = K \int_{0}^{\infty} N(R) V(R) \phi^{2}(hR) \, dR \tag{1} \]

where \( I(h) \) is the scattered intensity, \( h \) is the scattering angle \( \frac{4\pi \sin \theta}{\lambda} \), \( N(R) \) is the number of particles having radius \( R \), \( V(R) \) is the volume of particles having radius \( R \), and \( \phi \) is the single-particle scattering function \( \phi(R) \) for spheres of radius \( R \). \( K \) is a normalizing constant chosen so that \( I(0) = 1 \).

The program subsequently uses

\[ J(h) = 1/I(0) \int_{0}^{\infty} I(h^2 + z^2)^{1/2} \, dz \tag{2} \]

to calculate the slit smeared intensity \( J(h) \) which is also normalized to \( J(0) = 1 \).

For quantitative comparison of observed and calculated scattering, results were expressed as a function of a quantity \( hR_{0} \) where \( R_{0} \) is determined by the form of the distribution \( N(R) \). This procedure is identical to that described by Roess and Shull. A plot of \( \ln J \) vs. \( \ln h^2 \) for the observed scattering, superimposed on a calculated \( \ln J \) vs. \( \ln (h R_{0})^2 \) plot, determines \( R_{0} \) by noting coincident abscissae.

First calculations assumed a Gaussian distribution of the form

\[ N(R) = \exp \left( - \frac{(1 - R/R_{0})^2}{2\sigma^2} \right) \]

where \( \sigma \) is the standard deviation. No superposition could be obtained for \( \sigma = 0.1 \) to 0.5. A second calculation utilized a Gaussian volume distribution \( N(R) = \exp \left( - \frac{(1 - V/V_{0})^2}{2\sigma^2} \right) \). This attempt was also unsuccessful, as were rectangular, Maxwellian, and triangular size distributions (Table 1). In all these trial
calculations, the nature of the failure to superpose indicated a higher ratio of small to large pores. A $1/R^2$ distribution was tried with much more satisfactory results. Eventually nearly perfect superposition was obtained with a $N(R) = 1/R^2$ between 0.75 $R_o$ and 3.75 $R_o$, $N(R) = 0$ for $R < 0.75 R_o$ and for $R > 3.75 R_o$. Some of the trial scattering curves are shown in Figures 4 and 5. The final superposed experimental and calculated curves are shown in Figure 6.

The agreement shown in Figure 6 leads to a value of $R_o = 235 \text{ Å}$. Pore radii as determined by small angle scattering then range from 175 Å to 875 Å (350 Å to 1750 Å diameter) with the number varying as $1/R^2$.

Comparison of these results with TEM micrographs is instructive. Figures 7 and 8 show portions of the pore microstructure. As predicted, there are comparatively few very large pores and a great many smaller ones. The size distributions obtained by the two methods are compared in Figure 9. It can be seen that the correspondence is excellent and the two examination techniques are truly complementary.

SUMMARY

Small angle x-ray scattering curves of irradiated and annealed boron carbide have been analyzed by an extension of the Roess and Shull technique. Particle size distributions were varied through a series of computer-derived scattering curves until a good match was found between observed and calculated curves. The success of this method is contingent upon: 1) the particles being of known shape, 2) absence of interparticle interference; and 3) absence of multiple scattering. The pore size distribution obtained in this way corresponded favorably with that derived from electron micrographs.

ACKNOWLEDGEMENTS

The computations of scattering and slit correction were done with programs prepared by Mr. W. F. Hodgson. The electron micrographs were made by Mr. B Mastel. The authors gratefully acknowledge the contributions of these individuals.
REFERENCES


### TABLE I

**TRIAL DISTRIBUTIONS N(R) FOR SAS CALCULATIONS**

<table>
<thead>
<tr>
<th>Type</th>
<th>Equation ((X = R/R_0))</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectangular</td>
<td>(N(R) = 1, \alpha &lt; X &lt; 1) (= 0, X &lt; \alpha, X &gt; 1)</td>
<td>(\alpha = 0, 0.2, 0.4, 106)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.8, 1.0)</td>
</tr>
<tr>
<td>Gaussian</td>
<td>(N(R) = \text{Exp} - (1 - X)^2/2 \sigma^2)</td>
<td>(\sigma = 0.1, 0.2, 0.3,)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.4, 0.5)</td>
</tr>
<tr>
<td>Gaussian Volume</td>
<td>(N(R) = \text{Exp} - (1 - X^3)^2/2 \sigma^2)</td>
<td>(\sigma = 0.5, 1.0, 1.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.0, 2.5)</td>
</tr>
<tr>
<td>Triangular 1</td>
<td>(N(R) = \frac{(X - \sigma)/(1 - \sigma)}{\sigma^2}, \sigma &lt; X &lt; 1) (= 0, X &lt; \sigma, X &gt; 1)</td>
<td>(\sigma = 0, 0.2, 0.4, 0.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.8)</td>
</tr>
<tr>
<td>Triangular 2</td>
<td>(N(R) = \frac{(1 - X)/(1 - \sigma)}{\sigma^2}, \sigma &lt; X &lt; 1) (= 0, X &lt; \sigma, X &gt; 1)</td>
<td>(\sigma = 0, 0.2, 0.4, 0.6,)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.8)</td>
</tr>
<tr>
<td>Maxwellian Mass</td>
<td>(M(R) = X^m \text{Exp} - X^2) (N(R) = X^{m-3} \text{Exp} - X^2)</td>
<td>(m = 0, 0.5, 1.0, 1.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.0, 2.5, 3.0)</td>
</tr>
<tr>
<td>Inverse Square</td>
<td>(N(R) = \frac{1}{X^2}).</td>
<td>(X = 0 - 1, 0 - 2, 0 - 3,)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0 - 4, 0 - 5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(X = 0.5 - 1.5, 0.5 - 2.5,)</td>
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<tr>
<td></td>
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<td>(0.5 - 3.5, 0.5 - 4.5,)</td>
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<td>(0.5 - 5.5)</td>
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<td></td>
<td>(X = 0.75 - 1.75, 0.75 - 2.75)</td>
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<td>(0.75 - 3.75, 0.75 - 4.75,)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.75 - 5.75)</td>
</tr>
</tbody>
</table>
EXPERIMENTAL SCATTERING FROM BORON CARBIDE
IRRADIATED AT 500°C

COUNTS PER SECOND

IRRADIATED, ANNEALED 1800°C
AS IRRADIATED
NO SAMPLE

SCATTERING ANGLE, MINUTES

FIGURE 1
RECTANGULAR DISTRIBUTION OF RADII

N(R) = 1, \( a < R < R_0 \)

\( a = R_0 \)

\( a = 0 \)

GAUSSIAN DISTRIBUTION OF RADII

N(R) = \( \exp \left( -\frac{(R - R_0)^2}{2\sigma^2} \right) \)

\( \sigma = 0.1 \)

\( \sigma = 0.3 \)

\( \sigma = 0.5 \)

OBSERVED
**GAUSSIAN DISTRIBUTION OF VOLUMES**

\[ N(R) = \exp\left(-\frac{1-V/V_0}{2\sigma^2}\right) \]

**MAXWELLIAN MASS DISTRIBUTION**

\[ M(R) = \left(\frac{R}{R_0}\right)^n \exp\left(-\frac{R}{R_0}\right)^2 \]

\[ N(R) = \left(\frac{R}{R_0}\right)^{n-3} \exp\left(-\frac{R}{R_0}\right)^2 \]

\( n = 0.5 \)
\( n = 1.0 \)
\( n = 2 \)
\( n = 3 \)

*Observed*
N(R) BY SAS AND TEM IRRADIATED AND ANNEALED B₄C

PORE DIAMETER, ANGSTROMS