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THE EFFECT OF MATERIAL VARIABLES ON THE IRRADIATION PERFORMANCE OF BORON CARBIDE

By

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Abstract

Boron carbide pellets were fabricated with variations in material parameters. These pellets were irradiated in the Experimental Breeder Reactor-II (EBR-II) to determine the effect of these variations on the performance. Helium release from the material and swelling of the pellets are the primary measures of performance. It was determined that material with a smaller grain size released more helium and swelled less. The pellets with boron-to-carbon ratios greater than 4 to 1 did not perform well. Iron additions improved the performance of the material while density variations had little effect.

Key Words

Boron carbide, neutron absorber, swelling, helium release, material variations, irradiation performance.

Introduction

Boron carbide is being used as the neutron absorber material in liquid metal breeder reactor control systems because of its moderate cost, availability, compatibility with other components, and most importantly, because of the high neutron cross section afforded by ^{10}B atoms. Boron carbide is typically employed as hot-pressed pellets encased in stainless steel tubes. Pellet temperatures during irradiation can vary from 500°C up to 1200°C, and total neutron captures can exceed 60×10^{20} captures/cm^3. The neutron captures in the boron carbide result in the formation of helium and lithium atoms which are partially retained within the parent material. These reaction products and the incident neutron flux result in structural damage which influences the rate of helium release, as well as swelling and various physical properties. Since these phenomena can affect the performance of an absorber pin, they must be quantitatively assessed in relation to material parameters.

The results of numerous irradiation experiments[1-4] on the reference FFTF absorber material ($B_{4.0}C$ pellets with a density 92% of the theoretical value) have been reported. The present investigation addresses the material variables which could potentially influence irradiation performance of boron carbide. Variations in stoichiometry, grain size and density can occur as a result of fabrication, and can either improve or detract from boron carbide's performance in absorber elements. This paper describes the irradiation behavior observed in boron carbide pellets as a function of variations in stoichiometry, density, iron content and grain size.

Experimental

All of the boron carbide pellets in the BMV-2 Experiment were irradiated in Row 7 of the Experimental Breeder Reactor (EBR-II). The irradiation exposures were at three levels; the shortest was 127 full power days (FPD) and the longest was almost 300 FPD. Neutron fluences were as high as 6×10^{22} n/cm^2 ($E > 0.1$ MeV) and maximum neutron capture levels in boron carbide reached 63×10^{20} captures/cm^3.

The experimental capsules were composed of two separate, hermetically sealed, top and bottom sections. Each section contained a 16 cm-long section of boron carbide pellets, and gas plena were provided in both sections to accommodate the helium released during irradiation.

The capsule design included multiple encapsulation of the pellets by concentric stainess steel tubes, as shown in Figure 1. The helium-filled gap between the primary and secondary tubes was sized to achieve mean pellet temperatures of either 760°C or 980°C.

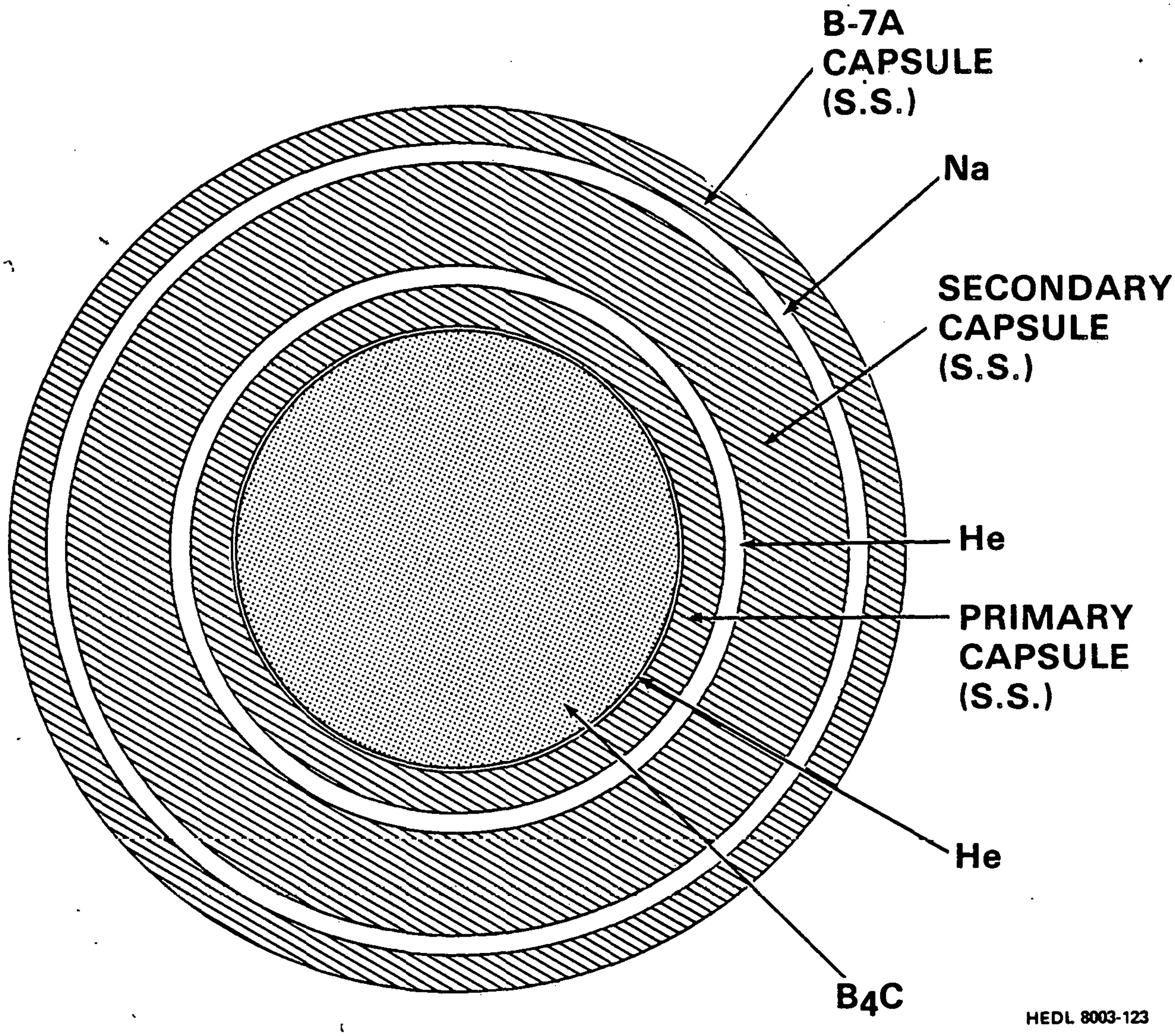

FIGURE 1. Cross Sectional View of Irradiation Capsule for Boron Carbide Pellet.

After irradiation, the outer tubes were removed and the inner tube was punctured by a laser, as shown in Figure 2. The helium gas in the capsule's plenum expanded into a known volume, and the pressure was measured by a manometer. Compositional analysis of the gas was performed, and the amount of helium released from the pellets during irradiation was determined. Subsequent vacuum fusion analyses of individual boron carbide pellets provided a measurement of helium retained within the parent material. Summation of the quantities of helium released and retained established the total amount of helium generated during irradiation, and therefore, the burnup.

Swelling measurements were made by simple dimensional characterization prior to and after irradiation. Identity of individual pellets within the pins was maintained, so the swelling was determined for each pellet.

Material

Hot-pressed boron carbide pellets (0.87 cm diameter) with a range of material variations were fabricated specifically for this irradiation experiment. The properties of the materials used in this experiment are listed in Table 1. The reference material possesses a density of 92% of that theoretically possible, and is nearly stoichiometric $B_{4.0}C$ with a grain size of less than 20 μm. In order to increase the ^{10}B neutron capture rate of this material in EBR-II, the starting powder was enriched to ~92% ^{10}B, compared to a nominal composition of 20% ^{10}B in naturally occurring boron.

Boron carbide possesses an appreciable range for a compound that extends from $B_{4.0}C$ to $B_{6.5}C$ ($B_{13}C_2$).[5] Powder and pellets with B/C ratios near 4.0 are easily produced. Boron carbide pellets with high B/C ratios were fabricated by hot-pressing, in graphite dies lined with boron nitride, a mixture of $B_{4.0}C$ powder and pure boron (92% ^{10}B content). A lack of

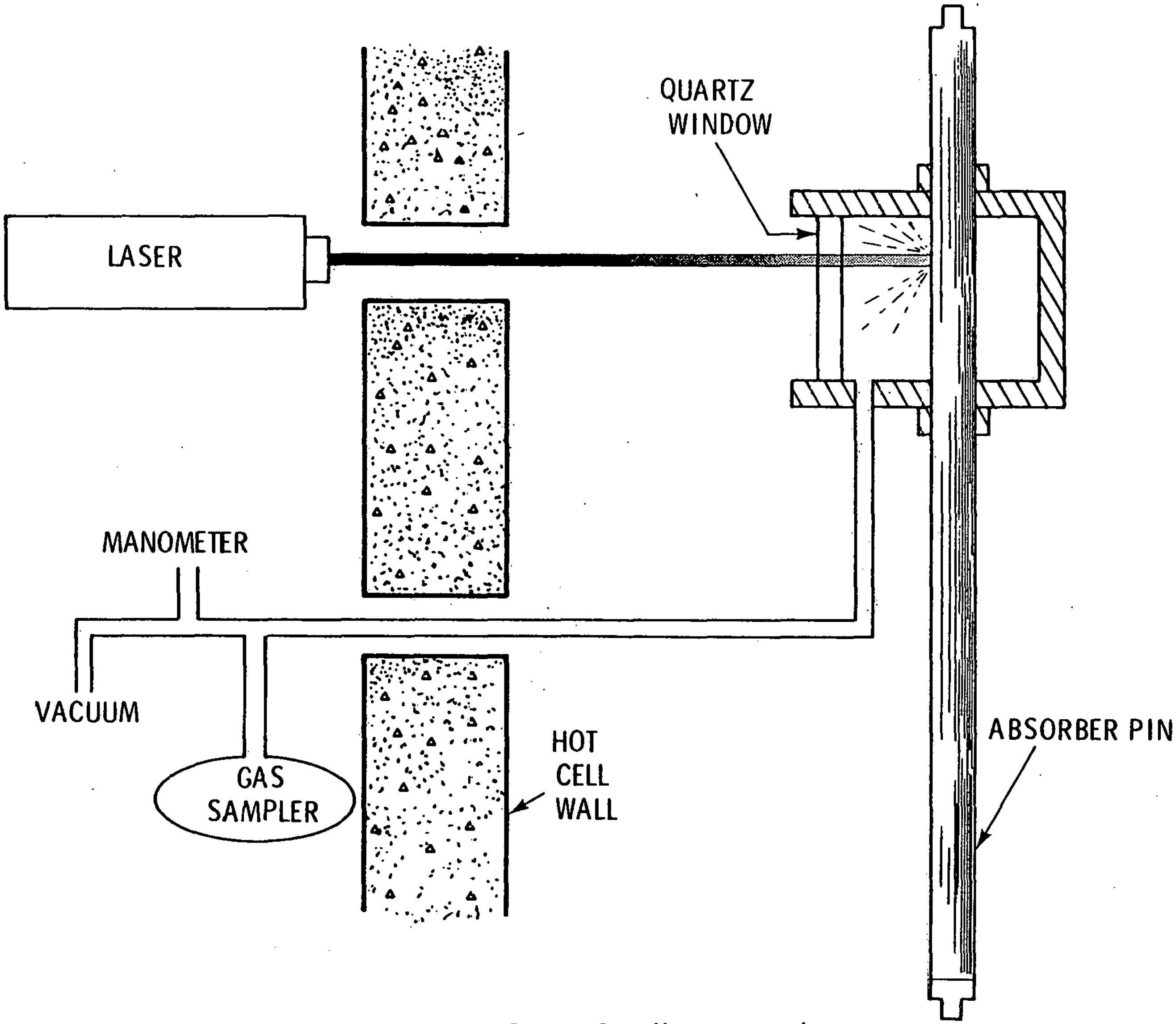

FIGURE 2. Laser Puncturing Device for Plenum Gas Measurement.

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TABLE I

BORON CARBIDE MATERIAL PROPERTIES

B_4C IDENTIFICATION	DENSITY (% OF THEORETICAL)	^{10}B IN THE BORON (%)	B/C RATIO	GRAIN SIZE (μM)
REFERENCE	92.1 ± .1	92.4	3.97	17
HIGH DENSITY	97.7 ± .2	92.4	3.99	22
LOW DENSITY	82.2 ± .1	92.4	3.92	16
LARGE GRAINED	91.5 ± .4	92.4	4.00	35
HIGH B/C (5.2)	91.4 ± 1.0	92.2 ± .1	5.22 ± .04	10
(6.5)	92.2 ± .3	88.0 ± 1.2	6.37 ± .13	14-21
IRON (1.46% FE)	93.9	92.4	3.97	21

homogeneity and a reaction between the pellet and the die plagued the fabrication of the high B/C material. By grinding, the reaction layer was removed, and pellets of acceptable quality were obtained.

In the specification of boron carbide pellets for use in breeder reactor absorber pins, material variables such as pellet density, grain size, and impurity content should be limited to ranges which provide acceptable performance. Pellet density is important from a design standpoint in determining total assembly weight and ^{10}B content, so in this experiment the impact of density (98% to 82% TD) on pellet irradiation performance was investigated. Likewise, grain size is a product of the fabrication processes which are used. Typically, boron carbide absorber pellets possess a grain size of 10 to 20 μm, but in this investigation, pellets with an average grain size of 35 μm were included in order to evaluate the effect of this parameter on performance. Finally, iron contamination is difficult to avoid in the fabrication of boron carbide pellets. The impact of this impurity on absorber performance was evaluated by including pellets with 1.5% Fe mixed into the powder batch prior to hot-pressing. Some second phase concentrations were observed during microscopic examination of these pellets.

Results

Helium release and relative swelling values are presented in Table II for pellets of 82, 92, and 98% density irradiated to burnup values of 26 x 10^{20} captures/cm^3 at 760°C and 980°C. Gas release was nominally 20% of that produced in all the capsules except for the 82% TD at 980°C, which released 32% of the helium generated. In an earlier experiment,(1) helium release was continually measured on 2.5 cm-long pellet columns with densities ranging from 99 to 80% TD, and a similar relationship of helium release to pellet density was reported. In Table II, the swelling data also appear to possess little dependence on density, except again for the one capsule with 82% TD pellets at 980°C, which displayed notably less swelling with the higher helium release.

TABLE II

EFFECT OF DENSITY ON GAS RELEASE AND SWELLING

DENSITY (% T.D.)	TEMP. (°C)	BURNUP**	GAS RELEASE (%)	GAS RELEASE cm^3/cm^3 B_4C***	RELATIVE* SWELLING ΔD	RELATIVE* SWELLING ΔL
82.2	760	20	17.5	13.0	0.91	0.88
92.1	760	26	16.5	15.9	1.00	1.00
97.7	760	20	21.3	15.9	0.83	0.84
82.2	980	21	31.9	25.0	0.45	0.32
92.1	980	26	19.5	18.8	1.00	1.00
97.7	980	21	18.5	14.5	0.97	0.83

*92% AS BASELINE DENSITY

**UNITS OF 10^{20} CAPTURES/cm^3

***STP

The grain size of the boron carbide was found to influence both the helium release and swelling. In Figure 3, the normalized values of helium release are presented for both the BICM-1 and BMV-2 capsules (B.U. $\approx$ 40 x 10^{20} captures/cm^3). The helium release has been normalized with respect to the exact burnup levels that existed in the individual capsules. At temperatures near 800°C, the helium release is quite sensitive to grain size. At 8 μm the helium release is over three times that at 35 μm. Above and below this temperature, however, grain size does not appear to be as significant a factor. It is interesting to note that in previous data for helium release from boron carbide, there is a maximum at approximately 800°C, which corresponds with the grain size dependent temperature regime in Figure 3.

In Figure 3, the swelling data for boron carbide pellets with grain sizes between 8 and 35 μm are also presented. As in the case of helium release data, it was observed that swelling at 760°C and 825°C was sensitive to grain size, but was relatively independent of grain size at 740°C and 980°C when considering the data from both BICM-1 and BMV-2. At 760°C and 825°C, the larger grained (28 to 35 μm) material possessed twice the swelling rate of the fine-grained (μm) material.

In Figure 4, the helium release data from boron carbide pellets with B/C ratios of 4.0, 5.2 and 6.5 are presented and compared with the data at 812°C from the BICM-1 Experiment. The helium release from pellets in the BMV-2 Experiment with B/C ratios of 6.5 and 5.2 at a temperature of 760°C was similar to the helium release seen in the BICM-1 Test. In both cases, the helium release was 45 to 75%, which is much greater than the release from boron carbide with a B/C ratio of 4.0 (10 to 20%). At 980°C the boron carbide with a B/C ratio of 5.2 released helium at a rate which was almost as high as it was at 760°C. However, at 980°C, the pellets with a B/C ratio of 6.5 retained almost as much gas as the reference boron carbide. It should be noted that the (B/C = 6.5) material had almost twice the grain size of the material with a B/C ratio of 5.2 or the material in the lower temperature capsules with B/C = 6.5. Considering the potentially dominant

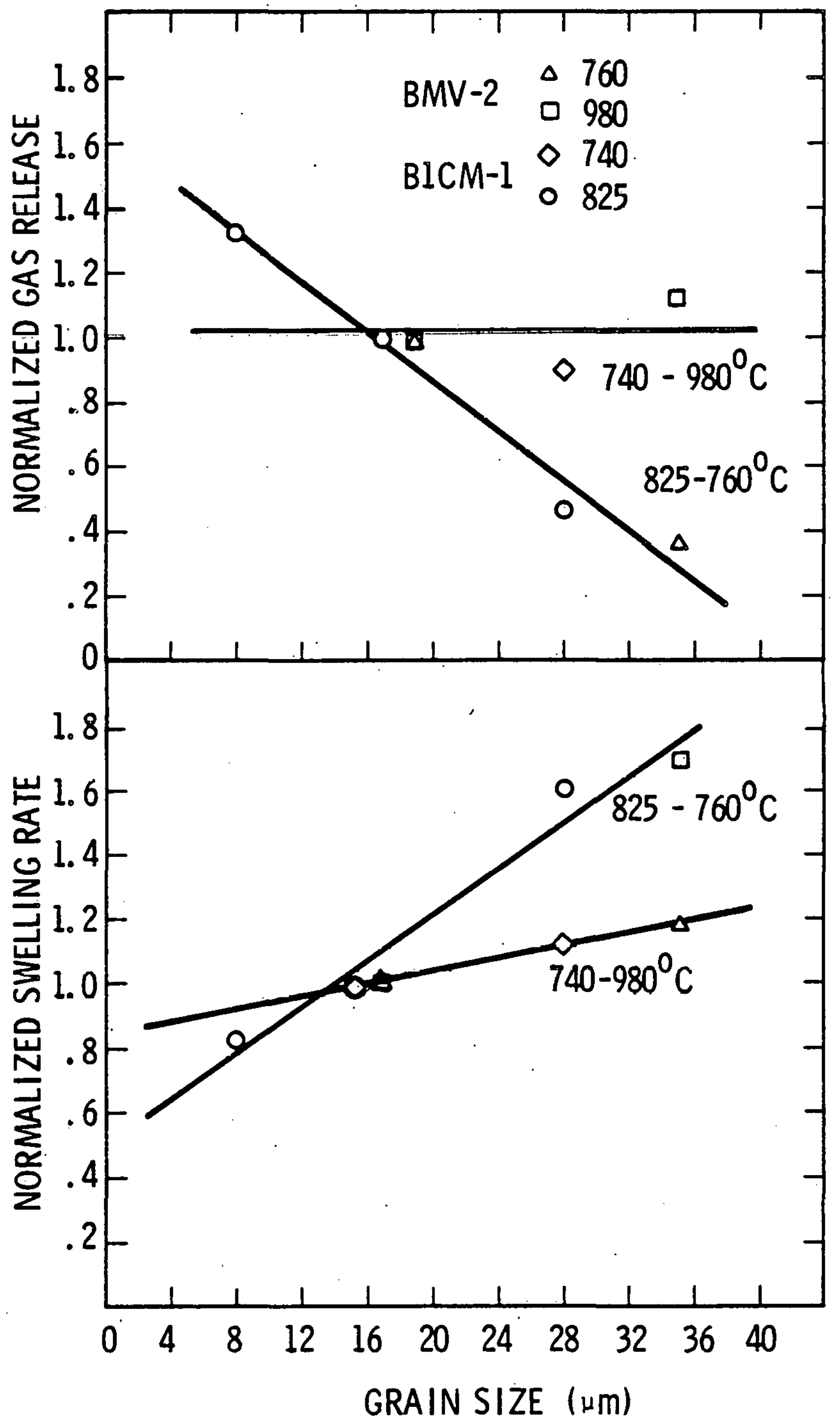

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FIGURE 3. Effect of Grain Size on Swelling and Helium Release

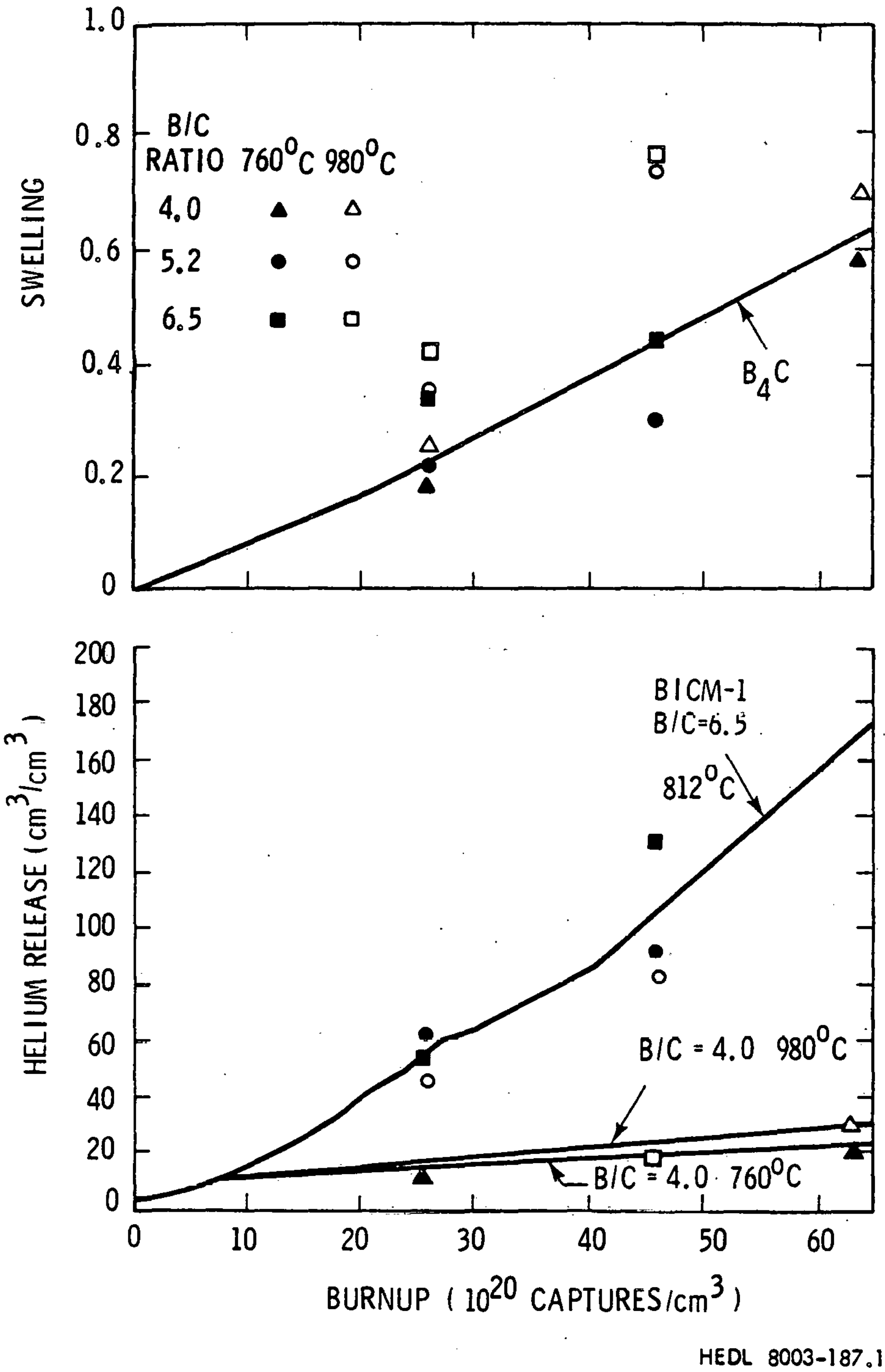

FIGURE 4. Effect of B/C Ratio on Swelling and Helium Release of Boron Carbide.

influence of grain size, it's difficult to distinguish a singular effect of B/C ratio. In Figure 4, swelling data are also presented for pellets with B/C ratios of 4.0, 5.2, and 6.5. At 760°C, the high B/C materials swelled at approximately the same rate as the reference material (B/C = 4.0). However, at 980°C, the high B/C ratio pellets exhibited swelling values which were almost twice those of the reference material. It should be noted again that the conditions favoring high swelling also induced low helium release.

In Table III, data are presented for iron-doped boron carbide and the nominally pure reference boron carbide. Both capsules operated at approximately 760°C: however, the doped material did not achieve as high a burnup level. The helium released from the doped material was actually lower than that released from nominally pure boron carbide. The relative swelling values in Table III do not distinguish any significant variation in swelling between the pure and doped material.

TABLE III

EFFECT OF IRON DOPING ON IRRADIATION PERFORMANCE OF BORON CARBIDE

Iron Content	Temp. (°C)	Burnup*	Helium Release (%)	Helium Release cm^3/cm^3 @ STP	Relative Swelling % ΔD	Relative Swelling % ΔL
1.5%	760	21	8.2	6.4	0.8	1.0
0.2%	760	26	16.5	15.9	1.0	1.2

*10^{20} atoms/cm^3

Discussion

Numerous investigations have been dedicated to understanding the phenomena associated with the swelling and helium release in boron carbide. From the accumulated data, a picture of the operating mechanisms has been developed.[6] Helium generation is thought to be the most important parameter in determining pellet performance. Once generated in the boron carbide matrix, the helium atoms can either: 1) diffuse to a grain boundary and eventually migrate to the plenum, or 2) cause nucleation or growth of a helium bubble within the bulk. The latter process is considered to be major cause of swelling in irradiated boron carbide, since the additional volume of the helium bubbles is reflected as a volume increase of the pellet.

Evaluating the data in this experiment as a whole, one feature becomes obvious: that is the interrelationship between the swelling and helium release demonstrated in Table IV. Temperature and material variables which enhance helium retention (i.e., decrease helium release) generally increase swelling, and vice versa. From the standpoint of a sealed pin design, this inverse relationship means that conditions that would yield longer helium release-limited lifetimes would at the same time shorten swelling-limited lifetimes. Consequently, trade-offs between these two design considerations would be required. An overall assessment of these data leads to the conclusion that, for reduced helium release, a larger grained material with some iron impurity would be optimum. On the other hand, for reduced swelling, a fine-grained material might be better. The specifications for boron carbide absorber pellets should avoid high B/C ratios. An appreciable amount of uniform iron impurity can be tolerated with no loss in performance.

From a mechanistic standpoint, the inverse relationship between swelling and helium release is easily appreciated. When the quantity of helium retained in the boron carbide is reduced (i.e., high helium release), the size and quantity of internal bubbles is also reduced. Since the cumulative volume of these bubbles determines the amount of swelling that exists, the bulk swelling would be less.

TABLE IV

EFFECT OF MATERIAL VARIABLES ON THE PERFORMANCE OF BORON CARBIDE

Material Variable		Helium Release	Swelling
Higher B/C Ratio	760°C	Higher	No Change
	980°C	No Change	Higher
Larger Grain Size		Lower	Higher
Lower Density		Slightly higher	Slightly Lower
Higher Density		No Change	No Change
Iron Content		Lower	No Change

(The above comparisons are made with respect to 92% theoretically dense boron carbide with a B/C ratio of 4.0, a grain size less than 20 μm and an iron content of 0.2%.)

The effect of pellet density on helium release appears to indicate that the grain boundary acts as a free surface for helium release. If diffusion along the boundary were to be a rate controlling mechanism, then the density changes from 98 to 82% TD would have significantly influenced the helium release rate. At 98% TD, essentially all of the pores are closed and diffusion of helium from the interior to the exterior of the pellet would be completely along the grain boundaries. But at 82% TD, most of the pores are open and interconnecting porosity provides a direct gas path to the pellet's surface. Since density did not play a major role in determining swelling or helium release, diffusion of helium to the grain boundaries appears to be more significant in determining helium release than diffusion along the grain boundaries to the pellet exterior.

From these results, grain size does appear to have a significant effect on helium release and swelling in a particular temperature range. Explaining the temperature dependence of this feature is difficult, but understanding the basic mechanism appears simpler. Actually, two processes may contribute: first, the smaller grain size material offers shorter distances for helium atoms to diffuse out of individual grains to a grain boundary. Secondly, the smaller grain size offers more grain boundary surface area. It has been observed that helium bubbles found in the bulk of individual crystallites are not present in the denuded region along a grain boundary.(6) It is believed that helium generated in the denuded region contributes to helium release even after bubbles are retaining helium in the bulk. The temperature dependence of this grain size effect may be linked to the dependence of bubble nucleation on temperature.

Since relatively little is known about the effect of B/C ratio on the physical and chemical properties of boron carbide, it is difficult to explain the effect of this variable on irradiation performance. The reduction in the helium release rate at higher burnup levels in Figure 4 for material with a B/C ratio of 4.0 is considered to be associated with the formation of helium bubbles. In the high B/C ratio material at 760°C the absence of a reduction in the helium release rate suggests that development or nucleation of helium trapping sites (bubbles) is depressed in the high B/C material.

At 980°C, the helium release rate of material with a B/C ratio of 6.5 was approximately the same as the reference material; however, the swelling was considerably more. In effect, this means that the helium in this high B/C ratio material produced a larger total of bubbles (and internal crack space). When considering the difficulty encountered during fabrication of these materials, it can be appreciated that they might have lower strength and, hence, be less capable of containing the helium gas in small bubbles.

Conclusions

Measurement of the irradiation performance of boron carbide pellets with a variety of material variables has determined that:

1. Boron carbide pellets with high B/C ratios did not perform as well as those with a ratio of 4.0.

2. Boron carbide pellets with smaller grain size displayed lower swelling, but higher gas release.

3. The density of boron carbide pellets did not have a significant effect on performance.

4. An iron impurity level of 1.5% did not detract from the performance, and resulted in lower gas release and slightly less swelling.

A summary observation is that grain size appears to be the most influential parameter that can be varied to affect irradiation performance of boron carbide. Smaller grain sizes release more helium and swell less. In a sealed absorber pin, however, enhancement of one of these factors would be at the detriment of the other.

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