Nano-scale microstructure damage by neutron irradiations in a novel Boron-11 enriched TiB_2 ultra-high temperature ceramic.

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Abstract

Ultra-high temperature transition-metal ceramics are potential candidates for fusion reactor structural/plasma-facing components. We reveal the irradiation damage microstructural phenomena in Boron-11 enriched titanium diboride (TiB_2) using mixed-spectrum neutron irradiations, combined with state-of-art characterization using transmission electron microscopy (TEM) and high resolution TEM (HRTEM). Irradiations were performed using High Flux Isotope Reactor at ~220 and 620 °C up to 2.4×10^{25} n.m^{-2} (E>0.1 MeV). Total dose including contribution from residual Boron-10 (^{10}B) transmutation recoils, was ~4.2 displacements per atom. TiB_2 is susceptible to irradiation damage in terms of dislocation loop formation, cavities and anisotropic swelling induced micro-cracking. At both 220 and 620 °C, TEM revealed dislocation loops on basal and prism planes, with nearly two orders of magnitude higher number density of prism-plane loops. HRTEM, electron diffraction and relrod imaging revealed additional defects on $\{10\bar{1}0\}$ prism planes, identified as faulted dislocation loops. High defect cluster density on prism planes explains anisotropic a-lattice parameter swelling of TiB_2 reported in literature which caused grain boundary micro-cracking, the extent of which decreased with increasing irradiation temperature. Dominance of irradiation-induced defect clusters on prism planes in TiB_2 is different than typical hexagonal ceramics where dislocation loops predominantly form on basal planes causing c-lattice parameter swelling, thereby revealing a potential role of c/a ratio on defect formation/aggregation. Helium generation and temperature rise from residual ^{10}B transmutation caused matrix and grain boundary cavities for the irradiation at 620 °C. The study additionally signifies isotopic enrichment as a viable approach to produce transition-metal diborides for potential nuclear structural applications.

Keywords: Titanium diboride (TiB_2); implantation/irradiation; transmission electron microscopy; high resolution TEM; ultra-high temperature ceramics.

1. Introduction

Novel high temperature materials, combined with advanced manufacturing routes, may offer game changing impacts on nuclear safety and engineering, particularly for future fusion reactors where operational conditions are significantly more challenging than those expected inside fission reactors [1]. Increasing the upper operating temperatures of nuclear reactors improves the power plant thermal efficiency [2]. However, the former is primarily limited by the melting temperature of structural materials. Additionally, an important safety criterion for structural materials in nuclear environments is the margin to melting [3], which ideally should be as high as possible. For these reasons, ultra-high temperature ceramic (UHTC) carbides, nitrides and diborides, which have melting temperatures more than 3000°C, are emerging as promising structural and high heat flux/plasma-facing candidate materials [4,5]. Diborides such as TiB_2 have hexagonal crystal structure and have been investigated for various non-nuclear applications ranging from wear resistant parts/coatings, cutting tools and aerospace based on excellent high temperature strength, high hardness, and good thermal shock resistance [6,7]. TiB_2 is also chemically inert and has good thermal conductivity [6]. For example, thermal conductivity of polycrystalline TiB_2 is 96-78 $Wm^{-1}K^{-1}$ between 20-1220 °C [6]. Further, TiB_2 is a medium to low atomic number (Z) material, implying desirable low impact on plasma power loss, if used in fusion reactors. Indeed, for fusion reactors, increase in plasma resistivity and power losses due to introduction of plasma contaminants from high Z materials is a critical issue [1,8]. In addition, TiB_2 can be chemically vapour deposited on many substrates that have envisaged nuclear applications such as tungsten, high chromium steels and titanium carbide [9], thereby making TiB_2 a good plasma facing wall coating candidate.

Successful implementation of new materials in high temperature nuclear environments demands a thorough understanding of irradiation-induced degradation processes. At present, little is known regarding the irradiation tolerance of TiB_2. Some results show irradiation-induced macroscopic changes in natural boron-based TiB_2 after light ion and neutron irradiations [10–12]. These macroscopic changes are typically light-ion irradiation-induced blistering/exfoliation or swelling and cracking due to in-reactor neutron irradiation. Low energy (5-120 keV) deuterium (D^+) and helium ($^4He^+$) ion irradiations at room temperature showed the exfoliation erosion yield to increase with ion energy [10,11]. Grinik et al. [12] observed macroscopic swelling of TiB_2 after neutron irradiations inside a WWR-M thermal nuclear reactor [13] at temperatures between 100-680 °C. Nearly 2-2.5 % swelling was observed for a fluence of ~0.3×10^{24} $n.m^{-2}$ at 100 °C. Macroscopic swelling was reported to increase with dose, reaching ~4-5% for ~2.5×10^{24} $n.m^{-2}$ fluence. The trend of macroscopic swelling with neutron irradiation temperature was reported to be non-monotonic in TiB_2 by Grinik et al. For example, ~3% swelling occurred at a fluence of 7×10^{23} $n.m^{-2}$ at 100 °C. With increasing temperature, swelling decreased steadily, reaching ~2% for the irradiation temperature between 400–530 °C for the same fluence. Beyond 600 °C, the authors observed a sharp increase in swelling, reaching 3% at 680 °C. The initial swelling at low temperatures is expected due to the well-known "point defect swelling" regime, prominent between the recovery stage I (onset of interstitial mobility) and stage III (onset of vacancy mobility) in ceramics [14]. This regime is typically characterized by swelling of the lattice parameter due to the accumulation of point-defects (PDs) and small interstitial atom clusters, thereby inducing macroscopic dimensional changes [14]. Maile et al. observed lattice parameter swelling of TiB_2 after neutron irradiations to temperatures as low as -166 and 24 °C using X-ray diffraction (XRD) [15]. Both a- and c-lattice parameters were reported to increase; however, with a larger change in the a-parameter as compared to the c-parameter. For example, the authors reported anisotropic a-parameter swelling of 0.46%, compared to 0.25% for c-parameter at -166 °C for the highest neutron fluence of 5×10^{21} $n.m^{-2}$. Maile et al. also showed that lattice parameter swelling of TiB_2 increased with neutron fluence between $(0.2\text{-}5)\times10^{21}$ $n.m^{-2}$. Anisotropic lattice parameter swelling-induced cracking of TiB_2 is also known to occur [12] and is a typical issue with hexagonal ceramics [16–18]. Grinik et al. mentioned cracking at the macro-scale with the extent decreasing with increasing irradiation temperature (100-400 °C). Above 500 °C, only grain boundary micro-cracks were reported [12,19]. Unfortunately, the neutron irradiation studies did not describe the associated evolution of defect microstructures, which is the key to understanding the macroscopic changes.

To the best of our knowledge, only one study has reported microstructural evolution due to irradiation in TiB_2 [20]. The authors reported that 200 keV electron irradiation in a transmission electron microscope (TEM) was sufficient to produce dislocation loops in electron transparent TiB_2 thin foils at room temperature. This was attributed to boron displacements, which have a low displacement threshold of ~20 eV [20]. Estimated net dose was 7 displacements per atom (dpa) of boron, at a dose rate of 10^{-3} dpa/s. The dislocation loops were less than 10 nm in diameter, lying on the basal (0001) planes.

The lack of understanding of the microstructure evolution of TiB_2 during irradiation is a fundamental knowledge gap that needs to be addressed to fully exploit its potential for high temperature nuclear applications. In this context, we have performed dedicated neutron irradiation of polycrystalline TiB_2 inside the mixed-spectrum High Flux Isotope Reactor (HFIR) at 210-230 and 610-630 °C, coupled with state-of-art post-irradiation microstructure characterization. The temperature evolution of irradiation-induced defects was studied using conventional TEM and scanning TEM (STEM). Additionally, high resolution TEM (HRTEM) imaging was also conducted to characterize irradiation-induced defects at the atomic scale.

It is important to highlight that natural boron consists of ~20% Boron-10 (^{10}B), which is well known to transmute by (n, α) reaction producing helium. This reaction cross-section is particularly large for thermal neutrons. Helium generation is deleterious for metals and ceramics because it induces matrix and grain boundary cavities/bubbles, leading to an early onset of void-swelling and high temperature helium embrittlement [21–26]. Additionally, progressive ^{10}B loss due to transmutation is also expected to compromise structural integrity. For example, Grinik et al. [12]. observed that surface layers gradually crumbled, representing loosely bound powders, after a neutron fluence of 2.5×10^{24} n.m^{-2} at temperatures greater than 530 °C in their natural boron-based TiB_2. However, if isotopically enriched Boron-11 (^{11}B) were used, the negative effects of ^{10}B transmutation could be avoided due to the much lower transmutation cross-section of ^{11}B to thermal neutrons [27]. Using this approach, polycrystalline TiB_2 samples were produced with 99.31 at.% isotopic enrichment in ^{11}B for the present study.

2. Experimental details

2.1. Material and neutron irradiations

Polycrystalline TiB_2 produced using isotopically enriched ^{11}B was fabricated by reaction hot pressing of ball-milled TiH_2 and 99.31 at.% ^{11}B (Ceradyne Inc. Boron Products) powders. The net concentration of boron in the samples was 28.4 wt.%, obtained from chemical analysis. The as-produced specimens consisted of predominantly TiB_2 grains, with titanium carbide inclusions (Ti_xC) on the grain boundaries. The average grain size of TiB_2 was 6.5 μm. Impurity element concentration in this material after fabrication is tabulated in Table 1, measured using DC plasma emission spectroscopy performed by Luvak Inc. Details about the material fabrication are provided in the supplementary materials.

Neutron irradiations were performed in the flux trap region of the 85 MW HFIR reactor at Oak Ridge National Laboratory (ORNL), USA. Disc-shaped coupon samples (6 mm diameter and 0.5 mm thickness) were irradiated inside sealed "rabbit" capsules. The target design temperatures for the capsules were 200 and 600 °C. For the targeted 200 °C irradiations, specimens were held inside holders fabricated from aluminium alloy Al-6061. For 600 °C irradiations, specimens were held inside vanadium-based V-4Cr-4Ti alloy holders.

Element	Al	Co	Fe	Hf	Mn	Nb	Si	V	W	Zr
Wt.%	0.014	0.015	0.014	0.022	0.013	0.034	0.013	0.015	0.013	0.58

Table 1: Impurity concentration in the specimens.

Specimens were irradiated simultaneously with various other ceramics in the capsule assembly as a part of an irradiation campaign. Each capsule was designed to accommodate thirty-two disc specimens, supported with SiC thermometry, retainer specimens and retainer springs. Two TiB_2 samples were sandwiched between rectangular SiC thermometry pieces for passive temperature estimation as shown in the schematic in supplementary materials. Specimen temperatures depend upon the axial location inside the reactor, fill gas and gap size between the specimen holder and outer housing. For both irradiations, the specimens were loaded ~6 cm above the reactor core centerline position. For the target 200 °C, helium was used as the fill gas, while 59.5% argon, helium balance was used for the 600 °C irradiation. Temperature contour plots of the loaded assembly cross-section and the disc specimens were predicted using finite element modeling (FEM) and are provided in the supplementary materials. Post-irradiation SiC thermometry [28] showed the actual temperature for the target temperature of 200 °C to be between 210-230 °C, while the actual temperature for the 600 °C target was between 610-630 °C. For convenience, the average irradiation temperatures will henceforth be noted as 220 and 620 °C. Because the capsules were at the same location inside the reactor, the net fast neutron fluence (E>0.1 MeV) for both irradiation temperatures was 2.4×10^{25} $n.m^{-2}$. The total irradiation time was nominally twenty-five days.

It is important to note that despite isotopic tailoring, ~0.69 at.% residual ^{10}B was present in the enriched powder. This would induce the $^{10}B(n, \alpha)^7Li$ transmutation reaction [27]. Apart from damage by fast neutrons, the recoil helium and lithium atoms from the (n, α) reactions also contribute to the total dose during the burn-out phase of ^{10}B in the beginning of the cycle (BOC). To assess the burnout of ^{10}B, the NJOY99 software code package was used with ENDF/B-VII.1 cross-sections for $^{10}B(n, \alpha)^{7}Li$ transmutation and 70-group neutron flux data taken from Ref. [29]. Displacement damage cross-sections were also used to determine the effective displacement damage energy deposition rates due to both fast neutron damage and damage from helium and lithium recoils. The ^{10}B depletion calculations predicted that the majority of ^{10}B burned out in the first five days and complete burn out occurred in the first ten days of irradiation. Net helium generated was ~0.42 at.%. Using the calculated effective displacement damage energy deposition rate and a displacement threshold of 40 eV for titanium [30] and 20 eV for boron [20], the final dose in displacements per atom (dpa), with sum of contributions from neutrons and (n, α) recoils, was ~4.2 dpa for both irradiation temperatures. Fig. 1 shows the evolution of dose and helium generation rate obtained from the neutronics calculations. The steep initial slope of dose and helium generation in Fig. 1 is the region of ^{10}B burn-out due to transmutation. Additionally, it is known that deposited energy associated with the recoils of ^{10}B transmutation can induce temperature rise. This temperature spike may not be detected by SiC thermometry because the former occurs during BOC, while the latter is mostly sensitive to the last few days of the irradiation. Using FEM, the peak specimen temperatures (occurring at BOC) were estimated to be ~330 °C for the irradiation at 220 °C and ~770 °C for the irradiation at 620 °C. About five days after BOC, the specimen temperatures were expected to return to the nominal values. More details about HFIR temperature controls, capsule designs and simulations of irradiation temperatures can be found in Ref. [31]

2.2. Post-irradiation specimen preparation and characterization

Following neutron irradiations, specimen preparation and characterization was conducted at the Low Activation Materials Development and Analysis (LAMDA) laboratory at ORNL. FIB lift-out specimens were prepared for TEM examination from irradiated samples and a reference non-irradiated material using a field emission gun (FEG) based FEI Versa3D Dual Beam™ FIB machine. The initial lift-out was performed using 30 keV gallium (Ga) ions. While thinning, the energy and current of the ion beam was progressively reduced to minimize milling induced defects. Final polishing of the foils was performed using 1 keV Ga ions. Conventional TEM and HRTEM characterization of the irradiation-induced extended defects was performed on FIB foils using a Schottky FEG based 200 kV JEOL 2100F TEM, equipped with a Gatan Orius high resolution CCD camera, a Gatan GIF Quantum imaging filter and a JEOL double tilt specimen holder. Additionally, high resolution scanning TEM (HRSTEM), streak (relrod) imaging and selected area electron diffraction pattern (SAED) analyses were also conducted using a state-of-art high-brightness XFEG based 200 kV FEI F200X Talos analytical STEM. Before performing TEM/STEM analysis, thin foils were checked using EDX mapping to distinguish between the TiB_2 and Ti_xC grains, the details of which can be found in the supplementary materials. Diffraction patterns were indexed using the Single Crystal™ pattern analysis software [32] .

Size and number density of extended defects were extracted from the TEM images. The diameter of loops was taken as the size of the defects. The error in size determination was estimated by repeated measurements on the TEM micrographs. For determining number density of observed defects, thickness of the foils was determined by an energy filtered TEM (EFTEM) thickness mapping technique using the Gatan GIF Quantum imaging filter and the log-ratio model [33]. Error in thickness determination by this technique is usually around ±20%, and hence constitutes the major fraction of error in the results. The error bars in number density of defects were estimated by a combination of statistical error in the number of defects considered for the analysis and the error in thickness measurement. As will be seen in the results section, cavities were also detected by TEM in the higher temperature irradiated specimens. Through-focal series imaging technique [34] was utilized to image the cavities. In this technique, when the objective lens of the TEM is under-focused, cavities appear bright with a dark Fresnel fringe around, and vice-versa. Cavity swelling was estimated by calculating the volume fraction of cavities observed in TEM micrographs. The main sources of error in calculating cavity swelling were in the thickness determination of the analyzed region, statistical error in the number of cavities in the analyzed zone and the error in cavity size determination. As mentioned previously, the error in thickness was about ±20% and was the major fraction of error. For faceted cavities, the longest distance was considered as the size, while for spherical cavities, the size is represented by their diameter. We must highlight that due to low displacement threshold energy of boron, it has been shown previously that even 200 keV electrons may induce matrix damage in natural boron based TiB_2 [20]. Because isotopic enrichment in ^{11}B is not expected to change the displacement threshold energy, characterizing the neutron irradiated samples by TEM may induce damage to the microstructure that may get mixed with the damage created by the neutrons. This situation is important to consider especially if the defect sizes expected from the neutron irradiations are small (less than a few nm, typical for low temperature irradiations). To avoid/minimize this issue, wherever possible, relatively large grains were selected for TEM analysis which had allowed the diffraction conditions to be adjusted on side of the grain for dislocation loop analysis while the images were recorded from the other side and with as small exposure times as reasonably possible. This is only important for characterizing dislocation loops and not for characterizing cavities because (i) cavities are imaged away from diffraction condition with an out of focus objective and (ii) 200 keV electrons at room temperature are not expected to induce any cavities.

3. Results

3.1 Evolution of irradiation-induced defects with temperature

3.1.1. Conventional TEM analysis of dislocation loops

Conventional diffraction contrast TEM characterization revealed irradiation-induced extended defects such as dislocation loops and black-dot damage after irradiations at both 220 and 620 °C. Fig. 2 presents bright field and low angle annular dark field (LAADF) STEM images of the same zone for the specimen irradiated at 220 °C. Imaging was performed using [0001] type diffraction vector close to the $[1\bar{2}10]$ zone axis. The extended defects were identified to be dislocation loops on the basal planes. In hexagonal materials after irradiation, loops usually form either on the basal planes with Burgers vector parallel to c-axis (basal c-type loops), or on the prism planes. Dislocation loops with mixed c- and a- components are also noted in some occurrences [35]. Using the **g•b** invisibility criteria [34], dislocation loops can be distinguished, provided they are sufficiently large, so that they can be tracked on images obtained with different diffraction vectors (**g**). In conventional TEM imaging, dislocation loops with Burgers vector parallel to c-axis will be in contrast for *{hkil}* reflections with a non-zero *l*, and will be invisible or show weak residual contrast for *{hki0}* reflections. On the other hand, prism plane loops, having predominantly a-axis component in Burgers vector, can be imaged when *{hki0}* reflections are operating. Thus, an identification between basal and prism loops can be made if the same area is imaged using *{hkil}* and *{hki0}* reflections. In our study, microstructures for 220 and 620 °C irradiated specimens were imaged by tilting the foil close to $[1\bar{2}10]$ zone axis, so that <0001> and $< 10\bar{1}0 >$ type diffraction vectors were available. Fig. 3 shows the dislocation loops detected using two-beam kinematical bright field (KBF) TEM imaging using [0001] and $[10\bar{1}0]$ diffraction vectors for both the irradiation temperatures. For 220 °C, a certain family of dislocation loops comes in contrast using [0001] reflection, in Fig. 3a. Tilting the same area to select the $[10\bar{1}0]$ diffraction vector made these loops invisible (Fig. 3b), while a new family of dense "black-dot damage" were visible. Based on this, dislocation loops in Fig. 3a imaged using [0001] reflection, had Burgers vector parallel to c-axis, and hence were basal plane c-type dislocation loops. The orientation of these loops was close to edge-on configuration in Figs. 2 and 3a, which suggests that their habit plane is (0001). This means (0001) type basal loops were pure edge in character. It should be noted that in Figs. 2 and 3a, the loops were not perfectly in edge-on configuration because the specimen was slightly tilted away from the zone axis to adjust the two-beam conditions. The dense black-dot damage in Fig. 3b was in contrast when $[10\bar{1}0]$ diffraction vector was selected and was invisible or in residual contrast when [0001] reflection was used for imaging. This means that these black-dots had an a-axis component in their Burgers vector and should be prism plane loops. The two most likely possibilities are $[2\bar{1}\bar{1}0]$ or $[10\bar{1}0]$ type loops. One requires another *{hki0}* imaging condition to clearly distinguish their Burgers vector based on unique visibility-invisibility patterns. However, for such small black-dot defects, it is nearly impossible to track them in images obtained using different tilts. Therefore, their exact Burgers vector was difficult to determine. Nevertheless, as mentioned previously, they are expected to be the prism plane loops having a-component in their Burgers vector.

Similar microstructures were observed for the specimen irradiated at 620 °C, with no significant evolution of the dislocation loops in terms of either size or number density (Figs. 3c and 3d). At 220°C, the average diameter of basal loops was 8.3±0.6 nm and the number density was (3.86±1.2) x10^{21} m^{-3}. Results extracted from TEM images are plotted in Fig. 4 where one can see that diameter of the basal loops was slightly more coarse at 620 °C; being 9.4±0.7 nm and number density being (1.43±0.8) x10^{21} m^{-3}. The size of black-dot prism loops at both 220 and 620 °C was between 2.5-3.2 nm but had almost two orders of magnitude higher number density (Fig. 4). For both irradiation temperatures, basal loops were larger, with a much lower density than the prism loops.

The nature of dislocation loops was not determined because of the complexity of the inside-outside technique [34] for very small size loops. However, vacancy mobility at the irradiation temperatures of 220 and 620 °C is not expected for high melting point ceramics. Based on this, all the dislocation loops are expected to be interstitial type.

3.1.2 HRTEM analysis and relrod imaging

HRTEM imaging and analysis of the diffraction patterns obtained from the irradiated specimens was conducted after irradiations at both 220 and 620 °C. Diffraction patterns obtained from the irradiated zone revealed streaks, which were parallel to $[10\bar{1}0]$ direction (<100> in three-index notation), with grains tilted to the $[1\bar{2}10]$ zone axis (Fig. 5). Centered dark field (DF) relrod TEM imaging was performed by selecting the streak using a small objective aperture. The corresponding TEM images (Fig. 6) of microstructure features inducing the streaks appeared as discontinuous bright lines on a relatively dark background. The lines or streaks seemed better developed after irradiation at 620 °C. To better understand these defects, atomic-scale HRTEM imaging was performed on the same irradiated specimens and a reference non-irradiated sample. The corresponding HRTEM images revealed linear defect features for both irradiation temperatures (Fig. 7). No such features were detected in the HRTEM images of the non-irradiated sample (Fig. 7e). The area of analysis of all the samples was tilted to $[1\bar{2}10]$ type zone axis in Fig. 7. Fourier transforms (FT) extracted from a part of the HRTEM images also revealed streaks, parallel to $[10\bar{1}0]$ direction and perpendicular to the linear defects detected in the HRTEM images. This revealed that the linear defects observed in HRTEM images and those detected in DF relrod images were the same type of defects, and they contribute to streaks in the diffraction patterns. These defects were lying on $\{10\bar{1}0\}$ prism planes as can be seen in Figs. 7a and 7c where the images are annotated with a dotted line representing the trace of $\{10\bar{1}0\}$ planes, identified from the FT. A bright field atomic-scale STEM image for the sample irradiated at 220 °C is shown in Fig. 8, where the defects on $\{10\bar{1}0\}$ planes were better resolved. Number density of these defects for both irradiation temperatures was similar, ranging between ~3.5-4.5x10^{22} m^{-3}. This additional loop density will increase the net defect density on the prism planes reported in Fig. 4 which only took into account the black-dot type defects detected by conventional TEM.

No evidence of irradiation-induced amorphization was detected for either irradiation conditions. This was inferred from the diffraction patterns recorded in the study where no amorphous rings were seen (Figs. 5-6). Further, HRTEM images in Figs. 7-8 also revealed a fully crystalline structure after irradiation.

3.1.3 Analysis of irradiation-induced cavities

TEM analysis revealed a homogeneous distribution of cavities in TiB_2 after irradiations at 620 °C. The average cavity diameter was 1.3±0.2 nm and the cavity number density was $(7.3\pm1.9)\text{x}10^{23}$ m^{-3}. BF under and over-focused images taken from areas tilted away from diffraction conditions are shown in Fig. 9, where a few identified cavities are highlighted in yellow circles. The magnitude of cavity swelling was estimated to be 0.12±0.05%.

When the specimen irradiated at 220 °C was analyzed, similar Fresnel type contrast was observed. BF under and over-focused images from the sample irradiated at 220 °C are presented in Figs. 9c and 9d. However, the identified objects were too small to be clearly interpreted (less than 0.5 nm), at the resolution limit of a TEM. At such small sizes, the contrast can be intermixed with similar Fresnel type contrast that can arise from surface roughness, surface contamination or even surface oxides. We, therefore, could not definitely identify these features as cavities.

For the specimen irradiated at 620 °C, TEM analysis also revealed extensive grain boundary cavities with size varying from 2-3 nm to as large as 20-25 nm. Larger cavities appeared faceted while smaller ones were spherical. BF under and over-focused TEM images of the largest cluster of faceted grain boundary cavities detected in the sample are shown in Figs. 10a and10b. In addition, Fig.10 also presents BF under and over-focused TEM images of another grain boundary that was decorated with smaller cavities (2-3 nm). At 220 °C, no grain boundary cavities were identified.

3.2 Grain boundary micro-cracks

At 220 °C, conventional TEM characterization revealed extensive irradiation-induced grain boundary micro-cracking, observed as fissures that were a few nm thick and that appeared much brighter in the TEM images compared to the matrix. A few BF TEM images of these cracks are shown in Fig. 11. Fig.11a shows a broad specimen overview revealing that most grain boundaries intercepted in the foil were cracked, as evident from the much brighter contrast. At 620 °C, microcracking improved significantly, with only one intercepted grain boundary in the foil showed some cracking, which is indicated in Fig. 11d. The fraction of cracked grain boundaries intercepted in the FIB foils was > 90% at 220 °C, and reduced to 10-20% at 620 °C. It must be noted that with an average grain size of 6.5 μm, only a few grain boundaries can be intercepted in a FIB foil. Because of this, the estimated cracked grain boundary fraction may vary depending on regions where the specimens are extracted from. Thus, these values should be regarded as a qualitative guide only.

Complementary transmission Kikuchi diffraction (TKD) analysis on the specimen irradiated at 220 °C was also performed and is included in the supplementary materials. Because the number of grains in FIB foil for tKD study was limited, the analysis did not specifically reveal a relation between the grain orientation, impurity Ti_xC phase and the extent of cracking.

4. Discussion

4.1 Dislocation loop microstructure evolution

Conventional TEM revealed irradiation-induced dislocation loops, lying along the basal (0001) planes with Burgers vector parallel to the c-axis and prism planes after neutron irradiations in HFIR at 220 and 620 °C. At both irradiation temperatures, basal loops were larger than the prism plane loops. However, number density of the prism plane loops was nearly two orders of magnitude higher. The prism plane loops were typical black-dot damage, while well-developed ring shaped/coffee-bean contrast was observed for the comparatively larger basal loops (see Figs. 2 and 3). The formation of dislocation loops implies that at least one kind of PDs are mobile at these temperatures. The dislocation loop microstructure was only slightly coarsened from 220 to 620 °C. In general, with most materials, an average loop size increase, and loop density decrease is expected with an increase in irradiation temperature [36]. However, the irradiation behavior and PD characteristics in ceramics are much more complicated than those in metals, because of factors such as differences in bonding type, presence of multiple sub-lattices, ionization effects, non-stoichiometry, and higher melting points, to name a few [37–39]. As a result, the formation and migration energies (E_f *and* E_m) of PDs in ceramics are usually significantly higher than in metals. For example, atomistic simulations show that E_m of silicon interstitials in 3-C SiC is ~1.53 eV, while the same for carbon interstitials is ~0.74 eV [40]. In contrast, E_m of self-interstitial atoms is less than 0.5 eV in most metals [41–44]. Thus, loop microstructures in ceramics typically are not expected to coarsen as fast with increasing irradiation temperatures as they do in metals. This can be seen in the neutron irradiation study of Katoh et al. [45], where black-dot damage dominated the microstructure of high-purity SiC for temperatures ≤ 800 °C, between 6-7.7 dpa. Similar results were noted for neutron irradiated BeO, where black-dot damage was prevalent up to 700 °C [46–48], while significant loop growth occurred at higher irradiation temperatures or due to post-irradiation annealing, above ~800 °C [47–49]. For TiB_2, to the best of our knowledge, no atomistic data are available on fundamental PD properties. Nevertheless, TiB_2 being an ultra-high temperature ceramic, one expects the PD migration barriers to be higher, as is the case for SiC. Therefore, no significant evolution of the dislocation loop microstructure between 220 and 620 °C, as observed in our case, is not surprising.

HRTEM and dark field relrod imaging in Figs. 6 and 7 showed extended defects in the microstructure, lying along $\{10\bar{1}0\}$ planes. These defects produced streaks parallel to $[10\bar{1}0]$ direction in the diffraction patterns. Similar features were not detected by HRTEM or in the diffraction pattern (FT) obtained from the reference non-irradiated sample (see Fig. 7e). This implies that these features were irradiation-induced. The streaks in diffraction patterns and in HRTEM images are typical of stacking faults associated with faulted dislocation loops [50–52]. Stacking faults generate streaks in the diffraction patterns due to diffuse electron scattering. These faults can be seen in contrast if the streak in the diffraction pattern is selected for imaging. It is intriguing and worth highlighting that these defects were longer (~4-10 nm) than the diameter of the black-dot damage (~2.5-3.2 nm) detected by conventional TEM for both irradiation temperatures (see Figs. 4 and 7). Thus, the size of black-dot defects, which are expected to be on prism planes, and the extended defects on $\{10\bar{1}0\}$ planes in Fig. 7 do not match with each other. This strongly suggests that the black-dot damage identified by conventional TEM in Fig. 3 and the defects identified by HRTEM are not the same type of defect clusters. From this, we infer that there is a second family of dislocation loops on the prism planes in TiB_2. We conclude that this second family of dislocation loops are faulted loops on $\{10\bar{1}0\}$ prism planes, and appear completely in edge-on configuration in the HRTEM images. These features were not fully revealed in the TEM images in Fig. 3 most likely because the defect microstructure was very dense, which can mask such fine details. The presence of dislocation loops on (0001) and $\{10\bar{1}0\}$ type planes in neutron irradiated TiB_2 is consistent with the known habit planes of dislocations observed in unirradiated TiB_2 [53].

No evidence of irradiation-induced amorphization of TiB_2 was found in our study. The presence of dislocation loops by 200 keV electron irradiations in the study of Carrard et al. [20] on TiB_2 to temperatures as low as room temperature and dose as high as 7 dpa suggest significant interstitial mobility at low temperatures. The authors also reported no sign of amorphization. Therefore, it appears that TiB_2 is an amorphization resistant ceramic and hence shares a similar trait with the other transition metal ceramics such as the carbides/nitrides of titanium/zirconium [25,54]

4.2 Effect of c/a ratio on dislocation loop microstructure

Irradiation-induced interstitial type defects are known to form in other hexagonal non-metals such as BeO, AlN, 6H-SiC, graphite, some MAX phases (Ti_3AlC_2, Ti_3SiC_2 and Ti_2AlC) and rhombohedral Al_2O_3. After neutron, ion and electron irradiations, the defect clusters that primarily form in these materials lie along the basal (0001) planes [17,47,62–66,48,55–61]. Dislocation loops on the prism planes are also reported, for example in BeO, but their fraction is reported as much smaller than basal loops over a wide temperature range [47,55]. In TiB_2, as evident from our study, a much higher number density of defects on prism planes were observed as compared to basal loops. This implies that prism plane loops are the most stable interstitial defect configuration for the irradiation temperatures in our experiments. Such microstructure evolution of TiB_2 demarks a significant difference from other hexagonal ceramics.

Another exception to the irradiated microstructure mostly dominated by basal loops in hexagonal ceramics is β-Si_3N_4 in which neutron irradiation results between 377–824 °C have shown that dislocation loops form only on $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes [52,57,67–69]. These dislocation loops are known to be faulted [52], producing similar contrast in HRTEM images as in TiB_2 (Fig. 7). Thus, in terms of dislocation loop microstructure, similarities exist between

TiB_2 and β-Si_3N_4, while all the other hexagonal materials mentioned earlier behave differently. We believe this behavior is not a coincidence and signals a potential role of the c/a ratio of hexagonal ceramics on the stability/type of irradiation-induced defects. c/a ratio determines which planes will be the most close packed [70]. The ideal c/a ratio for a hexagonal close packed (hcp) unit-cell produced by stacking monosized spheres is 1.633. In many ceramics, the c/a ratio can deviate significantly from this value because the unit cells may contain spheres of different sizes and with differing bonding characteristics. For β-Si_3N_4, the experimentally determined room temperature a-axis and c-axis lattice parameters lie in the range 0.7595-0.7608 nm and 0.2900-0.2911 nm respectively, thereby giving c/a ratio of ~0.38 [71]. This is an unusual relation between c- and a-axes leading to a very flat unit cell. For TiB_2, the c/a ratio is ~1.065 [6], ~35% smaller than the value for monosized spheres. Thus, even in the case of TiB_2, the unit cell is rather flat due to a significantly larger a-axis compared to the c-axis. Table 2 summarizes data of some hexagonal/rhombohedral materials which includes their lattice parameters, c/a ratios and primary dislocation loop habit planes. Materials like BeO and AlN deviate only ~0.6% and 2% respectively from the c/a ratio for monosized spheres. Experiments show that basal loops dominate in these materials [55,57]. For a significantly larger c-axis leading to a positive shift of c/a ratio towards higher values, for example in Ti_3AlC_2, Ti_3SiC_2, Ti_2AlC MAX phase ceramics, graphite and Al_2O_3, basal loops continue to dominate [58,62–64,66]. Once the c/a ratio reduces much below the value for monosized spheres, as in the case of TiB_2, prism plane loops dominate the dislocation loop microstructures. The dominance of prism plane loops is further exacerbated if c/a ratio decreases further. This is inferred from the case of β-Si_3N_4 in which, as mentioned previously, only prism loops form. In this case the c/a ratio of ~0.38 is ~4.3 times smaller than the value for monosized spheres. Qualitatively similar behavior is described in a review of hcp metals by Griffiths [70] where the primary loop habit planes are reported to be basal for large c/a ratios (eg. Zn, Cd), while prism plane loops start dominating as c/a reduces (eg. Co, α-Hf, α-Zr, Re, α-Ti, Mg). Griffiths [70] highlighted that prism planes will be the most close packed for c/a < ideal, while basal planes will be the most close packed when c/a > ideal. Using the argument that dislocation loops under irradiation tend to form on the most close packed planes, Griffiths and, Föll and Wilkens [70,72] proposed that basal plane loops are expected to be dominant when c/a ratio is large and prism plane loops are expected to dominate in materials with c/a ratios smaller than the ideal value, as observed in majority of hcp metals. It must be noted that this effect was proposed only for pure metals because impurities are known to modify dislocation loop microstructures [70]. We believe the data set on ceramics in the present study can, thus, be qualitatively explained using the same argument.

Material	Crystal structure	Lattice Parameters			Predominant loop habit plane	Lattice parameter swelling
		c (Å)	a (Å)	c/a		
Ti_3AlC_2	Hexagonal	18.562	3.073	6.040	basal	c swells; a shrinks
Ti_3SiC_2	Hexagonal	17.68	3.068	5.762	basal	c swells; a shrinks
Ti_2AlC	Hexagonal	13.65	3.0614	4.46	basal	c swells; a shrinks
6H-SiC	Hexagonal	15.117	3.0806	4.907	basal	c and a swell
α-Al_2O_3	Rhombo-hedral	12.991	4.7589	2.73	basal, minor prism fraction	c and a swell; higher c swelling
Graphite	Hexagonal	6.7	2.46	2.723	basal	c swells; a shrinks
hcp ideal	-	-	-	1.633	-	-
BeO	Hexagonal (wurtzite)	4.3792	2.696	1.624	basal, minor prism fraction	c and a swell; higher c swelling
AlN	Hexagonal (wurtzite)	4.982	3.112	1.600	basal	c swells; negligible a swelling
TiB_2	Hexagonal	3.2204	3.0236	1.065	prism, minor basal fraction	a swells; small c swelling
β-Si_3N_4	Hexagonal	7.595 - 7.608	2.900 - 2.911	~0.38	prism	-

Table 2. Lattice parameters, c/a ratio, habit plane of dislocation loops and lattice parameter swelling of some studied hexagonal and rhombohedral ceramics. Table generated using Refs. [6,35,66,67,69,71,73–78,47,52,55,57,61–63,65]

The results provide motivation for a systematic irradiation study involving various other hexagonal ceramics on which irradiation history is limited, for example ZrB_2, HfB_2, so that more elaborate data on the effect of c/a ratio on the observed loop microstructure can be acquired. Nevertheless, the comparison in the present study does reflect a role of c/a ratio on the dislocation loop microstructure development and the trend is similar to that reported in hcp metals.

4.3 Grain boundary micro-cracking

TEM analysis revealed extensive grain-boundary micro-cracks in TiB_2 after irradiation at ~220 °C. At 620 °C, the extent of microcracking was lower. Although, at this temperature grain boundary cavities were also observed, which made identification of cracks difficult.

Koyanagi et al. [78] analyzed the same HFIR irradiated isotopically enriched TiB_2 specimens as in the present study by scanning electron microscopy (SEM), which had also revealed grain boundary cracking but at SEM length scales. The authors also noted a reduction in cracking with increasing irradiation temperature from 220 to 620 °C. Therefore, the observation of micro-cracking by TEM characterization performed in the present study is qualitatively consistent with the observations of Koyanagi et al. at relatively larger length scales. Furthermore, these results are qualitatively consistent with neutron irradiation study of ^{10}B based TiB_2 by Grinik et al. [12] mentioned in the introduction where macro-scale cracking was observed for irradiation temperatures between 100-400 °C, while a significant improvement in cracking tendency was observed for temperatures higher than 500 °C. However, one major difference is that in the case of Grinik et al., where the samples were not ^{11}B enriched, a significant degradation of the samples after the neutron irradiations was reported where the surface layers crumbled like powders, which we expect to be induced by the pronounced ^{10}B loss due to (n, α) reaction. While no such significant sample degradation was reported by Koyanagi et al. (and in our study). This confirms that ^{11}B enrichment not only is beneficial to minimize deleterious effects of helium generation but may also improve structural integrity. Therefore, it appears that ^{11}B enrichment maybe an efficient pathway forward in utilizing boron based ceramic materials for nuclear structural applications.

We expect 220 and 620 °C irradiation temperatures to lie within the point-defect swelling regime of TiB_2. Because vacancies are not expected to be mobile in this regime, the strain due to excess formation volumes associated with PDs causes swelling of the lattice parameters, thereby leading to macroscopic crystallite swelling. For hexagonal ceramics having anisotropic unit cells, as shown in the previous section, interstitial type PDs and their clusters aggregate along certain preferred planes: basal or prism. Preferential presence of defects along certain planes causes anisotropic swelling of the lattice parameters. For example, a significantly larger c-axis swelling is reported after irradiations in BeO, AlN, Al_2O_3, and MAX phases, owing to excess interstitial type defects preferentially lying along (0001) basal planes [18,35,62,76,77,79] (see Table 2). Using XRD, Koyanagi et al. [78] reported much larger a-axis swelling and almost negligible c-axis swelling of the same 220 and 620 °C HFIR irradiated TiB_2 samples as in the present study. Similar results were reported by Maile et al. [15], mentioned in the introduction on natural boron-based TiB_2. These results can be attributed to the large fraction of interstitial type defects aggregated on the prism planes compared to basal planes, which was observed in our study. As a result of this anisotropic swelling, adjacent grains in differing orientations are expected to expand by differing amounts causing a misfit. The latter causes strain build up around such grain boundaries and the energy associated with it can develop micro-cracks. The extent of microcracking is expected to increase with the increasing magnitude of anisotropic swelling, which implies an increase in dose. Further, with increase in irradiation temperature, lattice parameter swelling typically decreases [14,79] implying improvement in cracking tendency. This behaviour is indeed visible in our study where micro-cracking improved significantly at the higher irradiation temperature and same results were reported by Koyanagi et al. [79]. Therefore, we believe that lattice strain induced by the PDs, that was measured by XRD by Koyanagi et al. on the same samples as us, is causing cracking.

To prove that lattice parameter swelling measured by Koyanagi et al. indeed caused the cracking observed in our study, we used the analytical model developed by Clarke et al. [18] that predicts the critical differential strain (misfit strain required to initiate spontaneous grain boundary cracks) using Griffith's equation for crack propagation. Per this model, the critical differential strain (ε_c) is related to the Young's modulus (E), boundary surface energy in the absence of anisotropic strain (γ), and the average grain diameter (2l) by Eqn 1. Spontaneous grain-boundary cracking is predicted if misfit strain exceeds the critical value obtained using Eqn. 1.

$$\varepsilon_c \sim \left(\frac{24\gamma}{El}\right)^{\frac{1}{2}} \qquad (1)$$

The grain boundary surface energy for TiB_2, to the best of our knowledge, is not detailed in the literature. But ~1 to 1.5 N/m are typical values of grain boundary surface energies in ceramics [80,81]. Therefore, it was assumed to be 1.5 N/m for TiB_2. Young's modulus (E) will depend upon the density (porosity) and chemical concentration of TiB_2. Munro et al.[6] have shown that higher TiB_2 mass fraction in the samples yield higher value of E. The authors note that when TiB_2 mass fraction exceeds 90%, E at 23 °C converges to ~565 GPa. E will change at higher temperatures, the value of which can be estimated using the analytical expression detailed by Munro et al. Using these values, the estimated critical differential strain is tabulated in Table. 3, along with the experimental differential strains based on a- and c- lattice parameter swelling values obtained by Koyanagi et al. [78]. As can be seen, the experimental strain is higher than the critical differential strain based on which Eqn. 1 predicts swelling induced cracking at both irradiation temperatures. This also supports the conclusion that anisotropic swelling caused the experimentally observed grain boundary cracking of TiB_2. These specimens contained Ti_xC impurities at the grain boundaries. Ti_xC being a high temperature ceramic is also expected to lie in its point-defect swelling regime for the present irradiation temperatures. Based on our TEM results and those obtained using transmission Kikuchi diffraction (tKD) provided in supplementary materials, it was not possible to conclude how Ti_xC grains would influence the swelling induced cracking in this case.

Temperature	ε critical	ε experimental
220 °C	4.4×10^{-3}	1.43×10^{-2}
620 °C	4.5×10^{-3}	1.0×10^{-2}

Table 3: A comparison of critical differential strain obtained by the analytical model proposed by Clarke et al. [18] with the experimental values for the two irradiation temperatures.

4.4 Evolution of cavity microstructure

A high concentration of homogeneously distributed small cavities (< 2 nm) were detected by TEM for the sample irradiated at ~620 °C (Fig. 9). Grain boundary cavities were also identified (Fig. 10). Migration energy for vacancies in high temperature ceramics is usually high [40,82]. Therefore, cavity or void formation at ~620 °C is typically not expected, unless there is a large concentration of gas like helium is introduced.

The powder used to fabricate the TiB_2 samples contained up to 99.31 at% ^{11}B. The remaining fraction was ^{10}B, which transmuted via (n, α) reaction, generating helium and providing additional dose from the recoils. Neutronics calculations in Fig. 1 show that this transmutation reaction is relatively fast and occurs within the first few days of the BOC. A majority of the helium generation and the associated dpa dose was imparted in the first five days, while a full ^{10}B burn out occurred within the first ten days. Accumulated dose only due to the recoils was ~2.2 dpa and helium generation was ~0.38 at% at the end of the first five days of BOC. At the end of complete burn out after ten days the dose was ~2.8 dpa and ~0.42 at.% helium was generated (Fig. 1), while the neutron dose was almost negligible. In this period, the He/dpa ratio was ~ 0.15 at.% He/dpa, which is extremely high. The slope of the dpa curve in Fig. 1a suggests nearly four times higher dose rate at BOC. Additionally, FEM modelling predicted ^{10}B transmutation at BOC caused a temperature spike in the specimen, reaching an average temperature of ~770 °C as compared to nominal temperature of ~620 °C (see supplementary materials). Therefore, this irradiation period can be considered as a situation of relatively high dose rate high temperature simultaneous dual irradiation, compared to the rest of the irradiation cycle. We believe the nucleation and growth of the high concentration of cavities primarily occurred during this BOC period due to the high concentration of helium, reasonable dpa dose and higher temperatures. The high number density of cavities and smaller cavity sizes are typical of the presence of helium, either pre-injected or injected simultaneously, thereby enhancing the cavity nucleation rate [21,23]. Given the amount of helium generated and relatively low overall dose, the cavities are expected to be mostly helium filled bubbles. Zinkle et al. [83] have shown that at low temperatures where vacancy mobility is not expected in ceramics, a helium concentration of around ~1 at.% is typically needed to nucleate cavities/bubbles. In our case, the helium generated is lower than 1 at.%, but the associated dpa dose and the high temperature is expected to assist some helium and/or vacancy mobility which may lead to cavity/bubble formation at lower helium concentrations. Role of helium is further exacerbated from the heterogenous cavity nucleation seen on grain boundaries (Fig. 10), and on pre-existing dislocations in the Ti_xC impurity phase (see supplementary materials). Without helium, cavities do not appear on typical microstructure sinks because the latter are PD annihilation sites. These arguments strengthen the hypothesis that the observed cavities formed primarily because of helium generation from the (n, α) reaction of residual ^{10}B and are not voids that form in the void swelling regime of the material. The magnitude of swelling induced by cavities (0.12±0.05%) remained much lower than the overall macroscopic swelling of 0.81% reported by Koyanagi et al. [78] on the same irradiated specimen.

For the sample irradiated at 220 °C, Fresnel type cavity contrast was observed. But owing to small sizes (< 0.5 nm), TEM cannot unambiguously distinguish between real cavities or artifacts arising from surface roughness or surface impurities. Nevertheless, the results show that helium-induced cavity formation decreases as irradiation temperature decreases in TiB_2.

Grinik et al. [12] reported a sharp increase in swelling of natural boron-based TiB_2 under neutron irradiation between 550–700 °C, which resembled a typical swelling behavior of a ceramic transitioning from point-defect swelling to void-swelling regime [14]. This temperature window coincides with the irradiation temperature of 620 °C in our study where cavities were observed. However, the specimen would have contained ~20% ^{10}B, which is the natural abundance. The presence of ^{10}B is expected to cause a tremendous increase in sample temperature, much higher than the nominal temperature, due to the (n, α) recoils. Therefore, we believe that the results are not comparable to when samples are highly isotopically enriched in ^{11}B, as in our study. These results highlight that in boron containing materials, an estimation of temperature rise due to the $^{10}B(n, \alpha)^7Li$ reaction, subsequent dpa dose and helium generation must be considered to fully understand the irradiation behavior without ambiguities.

4.5 Synergistic effect of lithium generation on microstructure evolution – an open question?

Apart from generating helium, ^{10}B transmutation also produced $^{7}Li^{3+}$ isotope in the same amounts, i.e. ~0.42 at% lithium and would have the same generation curve as that for helium shown in Fig. 1b. This is a large fraction of lithium. Apart from solely being a recoil, lithium is a reactive alkali metal, known to strongly interact with elements like oxygen, nitrogen and carbon that are common impurities [84]. Lithium also chemically interacts strongly with various metal elements, including titanium [84] as has been demonstrated in Li-ion battery research. Lithium can also interact with boron to form Li_xB_y phases [85]. Therefore, important synergistic phenomenon of lithium with PDs may emerge during elevated temperature irradiation of materials containing ^{10}B. But knowledge of these processes is lacking. Recent atomistic simulations of point defects and transmutation products in ZrB_2, which is structurally similar to TiB_2 [86] predicted a strong binding between lithium and vacancies of both boron and zirconium. The authors reported higher trapping energies of lithium with vacancies compared to those predicted for interaction of helium and vacancies. Further, solubility of lithium in nuclear ceramics is not known. Stoto et al. [87] performed lithium ion irradiations on B_4C at 300 K. After irradiations to 16 dpa with a peak lithium concentration of ~20 at%, a homogeneous amorphous lithium phase formed. Below this concentration, the latter was not detectable by TEM. These limited results suggest a non-negligible contribution of lithium on irradiation effects. Hence, in the case of TiB_2, ~0.42 at% lithium may play a role on the microstructure evolution during irradiation. Therefore, an understanding of the irradiation response of TiB_2 under neutron irradiations can only be developed if lithium effects are addressed. However, detecting low Z elements like lithium by analytical TEM based techniques such as EDX and electron energy-loss spectroscopy (EELS) is a challenge, especially when the concentrations are low [88]. In the future, complimentary atom probe tomography experiments would be needed to examine the effects of lithium on the irradiation response of TiB_2.

5. Conclusions

Neutron irradiation response of ^{11}B enriched TiB_2 was studied at nominal temperatures of ~220 and 620 °C and neutron fluences up to 2.4×10^{25} n.m^{-2} (E>0.1 MeV). The dose, including the contribution from residual Boron-10 (^{10}B) transmutation recoils, was ~4.2 dpa. Microstructure characterization using TEM revealed irradiation-induced extended defects such as dislocation loops and cavities. At 220 and 620 °C, dislocation loops on basal and prism planes were identified, with the number density of prism plane loops nearly two orders of magnitude higher than basal loops. Faulted prism plane dislocation loops, lying on $\{10\bar{1}0\}$ planes, were also identified. The presence of both basal and prism plane dislocation loops is typical of hexagonal materials, but the higher fraction of prism plane loops in TiB_2 is a significant departure from results reported for other ceramics such as AlN, BeO, Ti_3AlC_2, Ti_3SiC_2, Ti_2AlC MAX phases, graphite, 6H-SiC and α-Al_2O_3 in which basal loops dominate. The c/a ratio of the hexagonal structure may control the dislocation loop microstructures with basal loops dominating for c/a close to ideal or larger. For c/a ratio much smaller than ideal 1.633, prism plane loops tend to dominate. Similar observations are reported previously for hcp metals.

TiB_2 suffers from anisotropic lattice parameter swelling induced micro-cracking. This was inferred from the observation of grain boundary micro-cracks, which decreased with increasing irradiation temperature. Further, the high number density of interstitial-type defects on prism planes in TiB_2 observed in the present study explains the much larger a-lattice parameter swelling of the unit cell that has been previously reported.

Helium generation and the temperature rise from transmutation of residual ^{10}B led to the nucleation of matrix and grain boundary cavities for the sample irradiated at 620 °C. At lower temperatures, the tendency to form helium induced cavities decreased. In general, like most materials, TiB_2 is susceptible to helium induced cavity formation. The study emphasizes that isotopic enrichment is a powerful tool to utilize transition-metal ceramic diborides for potential nuclear structural applications because it can minimize helium generation and may also prevent severe degradation of the material that may occur due to a progressive ^{10}B loss by (n, α) reaction.

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