Initial investigation of B₄C–TiB₂ composites as neutron absorption material for nuclear reactors

J. Wang, D. Ren, L. Chen, G. Man, H. Zhang, L. Luo, W. Li, Y.B. Pan, P. Gao, Y. Zhu, et al.

► To cite this version:

J. Wang, D. Ren, L. Chen, G. Man, H. Zhang, et al.. Initial investigation of B₄C–TiB₂ composites as neutron absorption material for nuclear reactors. *Journal of Nuclear Materials*, 2020, 539, pp.152275. 10.1016/j.jnucmat.2020.152275 . hal-02931972

HAL Id: hal-02931972

<https://hal.science/hal-02931972>

Submitted on 10 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ji Wang: Conceptualization, Methodology, Investigation, Writing – original draft, Writing - review & editing, Visualization. **Donglou Ren:** Methodology, Investigation, Writing – original draft, Writing - review & editing, Visualization. **LeiLei Chen:** Investigation, resources. **Guian Man:** Writing - review & editing, software. **Houyuan Zhang:** Writing - review & editing, software. **Hongpeng Zhang:** Investigation, resources. **Laihui Luo:** Conceptualization. **Weiping Li:** Conceptualization. **Yanbo Pan:** Resources. **Peifeng Gao:** Conceptualization, Methodology, Writing - review & editing, software, Funding acquisition, Supervision. **Yabin Zhu:** Conceptualization, Methodology, Writing - review & editing, resources, Supervision. **Zhiguang Wang:** Conceptualization, Methodology, Supervision, Funding acquisition.

Initial investigation of B₄C–TiB₂ composites as neutron absorption material for nuclear reactors

Ji Wang^{a, 1}, Donglou Ren^{b, 1}, LeiLei Chen^c, Guian Man^d, Houyuan Zhang^d,
Hongpeng Zhang^e, Laihui Luo^a, Weiping Li^a, Yanbo Pan^a, Peifeng Gao^{d, *},
Yabin Zhu^{e, *}, Zhiguang Wang^{e, *}

^aSchool of Physical Science and Technology, Ningbo University, Ningbo
315211, China

^bISCR (Institut des Sciences Chimiques de Rennes)-CNRS, UMR 6226,
Univ. Rennes, F-35000, Rennes, France

^cNingbo Institute of Materials Technology and Engineering, Chinese
Academy of Sciences, Ningbo, 315201, China

^dKey Laboratory of Mechanics on Western Disaster and Environment,
Ministry of Education, College of Civil Engineering and Mechanics,
Lanzhou University, Lanzhou 730000, China

^eInstitute of Modern Physics, Chinese Academy of Sciences, Lanzhou
730000, China

* Corresponding Authors: gaopf@lzu.edu.cn, zhuyabin@impcas.ac.cn,
zhgwang@impcas.ac.cn

¹ Ji Wang and Donglou Ren contributed equally to this work.

23 Abstract

24 In this study, a specifically designed B_4C - TiB_2 composite with the
25 typical microstructural feature of a TiB_2 network (cages) that
26 encapsulates a B_4C matrix was fabricated by the molten-salt and spark
27 plasma sintering (SPS) method. The finite-element (FE) calculation
28 results show that the connected TiB_2 cages constitute a thermally
29 conductive network, which effectively improves the overall thermal
30 conductivity of the composite; these results agree well with the
31 experimental results. Moreover, the Vickers indentation results reveal that
32 the TiB_2 network (cages) can effectively impinge/block the propagation
33 of cracks, which increases the composite toughness. The composite was
34 subjected to helium (He) ion irradiation to simulate the situation in which
35 the B_4C - TiB_2 composites serve as neutron absorption material, and for
36 which case a high quantity of He atoms is produced by the $B^{10}(n, \alpha) Li^7$
37 nuclear reaction. According to the transmission electron microscopy
38 (TEM) results, the interfaces between TiB_2 and B_4C act as effective sinks
39 for He atoms, and are preferential nucleation sites for He bubbles. The
40 theoretical and experimental results show that when the B_4C - TiB_2
41 composites serve as neutron absorption pellets in nuclear reactors, they
42 exhibit a better resistance to their disintegration than pure B_4C pellets.
43 Consequently, the performance of the control rods of nuclear reactors can
44 be improved.

45 Keywords: neutron absorber; B_4C pellet; He irradiation; crack
46 propagation; finite element.

47

Journal Pre-proof

1. Introduction

B_4C is widely used as a neutron absorption material for control rods (CRs) in many nuclear reactor systems, in particular in fast reactor systems [1] (e.g., Phenix (France), BN (Russia), JOYO (Japan), ALMR, FFTF (United States)) owing to its high melting temperature, outstanding thermal stability, good mechanical properties, and the high neutron absorption cross section of ^{10}B ; B_4C neutron absorbers play an important role regarding the performance of CRs by, for example, adjusting the reactivity compensation during the normal operation cycles of nuclear reactors, initiating/terminating an operation cycle for refueling or reactor component maintenance, and rapidly shutting down the reactor if abnormal conditions occur. Therefore, B_4C neutron absorbers are of primary importance for the safe and efficient operation of nuclear reactors.

In many CR designs (e.g., JOYO), B_4C materials are usually presented in the form of pellets. However, during the operation lifetime of CRs, B_4C pellets often fracture into pieces and even powders [2]. These fractured B_4C pellet pieces progressively fill the gaps between the pellets and cladding materials, which accelerates the absorber-cladding mechanical interaction [2]. This leads to an incompatibility between the cladding materials and other components of reactors (e.g., induced absorber swelling cladding cracking (IASCC)) and shortens the CR

lifetime. Moreover, the cracked materials are very sensitive to the subsequent radiation-assisted dissolution (i.e., radiolysis effects [3-5]). Regarding water-cooled nuclear systems, when cooling water leaks into the pellet capsule owing to IASCC-induced cracking [6], the radiolysis effect accelerates the dissolution of the absorber materials and promotes the disintegration of B_4C pellets [5]. Both effects degrade the CRs and safe operation of nuclear reactors.

According to previous research studies, the disintegration of bulk B_4C ceramic pellets is closely associated with the thermal-gradient-induced macrocracks and swelling-gradient-induced microcracks [7]. During the service lifetime of CRs, the (n, α) nuclear reaction releases an average energy of 2.78 MeV per event [1]; the most energy is deposited within the B_4C matrix. For instance, at a CR burnup of 10^{22} cap/cm³ per year, a volume power of 1.5×10^2 W/cm³ is deposited in the B_4C pellets. Owing to the low thermal conductivity of B_4C and the high heat-generation rate caused by the $^{10}B (n, \alpha) ^7Li$ reaction, the temperature gradient of B_4C pellets can reach up to 10^3 K/cm. Such a high temperature gradient causes a great thermal stress and results in thermal-stress-induced macrocracks. Moreover, a high quantity of He atoms produced by the transmutation reaction accumulate in the form of flat lenticular He bubbles [8,9]. These He bubbles cause significant volume swelling. When the neutron absorption pellets are placed in

thermal neutron reactors, owing to the self-shielding effect [7,10], the burnup of the pellet periphery is usually stronger than that of the interior. Because the He atom production is proportional to the burnup level, a gradient distribution of He bubbles leads to a steep swelling gradient of the B₄C material and an abrupt local strain [7]: the consequence are swelling-gradient-induced microcracks. In general, the released heat and He atoms produced by the $^{10}\text{B} (n, \alpha) ^7\text{Li}$ reaction are two factors that lead to the formation of cracks. Both factors promote the formation of macro-scale cracks and facilitate the crack propagation through pellets, which result in their disintegration [2,11].

Therefore, it is of vital importance to improve the thermal conductivity and irradiation-induced swelling resistance of B₄C absorber materials to guarantee the good long-term performance of CRs and a safe and efficient operation of nuclear reactors. B₄C–diborides composites have been explored a long time ago to improve the performance of B₄C in the irradiation field. For example, B₄C–HfB₂ composite was designed to improve fracture toughness [12, 13] and the thermal-mechanical properties of the neutron absorber [12]. In this study, a low economic cost and honeycomb-structured B₄C–TiB₂ composite was elaborated to attain the aforementioned objective. The main feature of the composite is a highly thermally conductive cage-like TiB₂ network that encapsulates conventional B₄C matrix grains. TiB₂ has a high melting point (3498 K),

exceptional hardness (25-35 GPa), highly thermal conductivity, excellent wear resistance, a low thermal expansion coefficient ($4.6 \times 10^{-6} \text{ K}^{-1}$, which is almost the same as that of B_4C , $4.5 \times 10^{-6} \text{ K}^{-1}$), and a high oxidation resistance [14-18]. Owing to the inimitable characteristics of TiB_2 , it is therefore selected as the cage-like structure of the B_4C – TiB_2 composites. The good features of conventional B_4C material are maintained, and the thermal conductivity of the composite is significantly improved with respect to that of the pure B_4C material. In addition, the composite exhibits many interfaces.

The B_4C – TiB_2 composites were subjected to He ion irradiation to simulate the situation in which the B_4C – TiB_2 composite is exposed to a high neutron flux, and a high quantity of He atoms is produced by the (n, α) reaction. Moreover, a series of post-irradiation analyses and FE calculations were conducted to evaluate the behavior of the B_4C – TiB_2 component in a nuclear reactor environment.

2. Experimental details

2.1. Material synthesis

A two-step synthesis method was employed to synthesize the B_4C – TiB_2 composite [19]. In the first step, Ti and B_4C powders were mixed with NaCl and KCl in an Al_2O_3 crucible. The mixtures with initial $\text{B}_4\text{C}/\text{Ti}$ molar ratios of 6:1, 4:1, and 2:1 were exposed to an Ar atmosphere at 1273 K. After the (1) and (2) in-situ reactions in the melted salt bath, a

uniform TiB_2 coating occurred on the B_4C particles. The remnant NaCl , KCl , and other impurities were washed away with deionized water, and the samples were subsequently dried to obtain dry TiB_2 -coated B_4C powders. Note that the melt point of NaCl and KCl mixing is low (~ 933 K) and the liquid mass transfer mode between B_4C and Ti in the molten salts guarantees the uniform nucleation and growth of TiB_2 on the surface of B_4C particles. Therefore, the NaCl and KCl were employed as the medium for reactions.

In the second step, the mixtures containing uniformly TiB_2 -coated B_4C powders with different TiB_2 contents were sintered in a spark plasma sintering (SPS) system (SPS-20T-15, Chen Hua) with the same procedure to obtain three cylindrical bulk samples with diameters of 13 mm and heights of 2 mm (denoted as S1, S2, and S3). In the SPS procedure, the heating rates are 50 K/min from RT to 1673 K, and 25 K/min from 1673 K to 1973 K, respectively. The holding time and temperature are 10 min and 1973 K, respectively. The pressure during the holding stage is 45 MPa. The cooling rate is 50 K/min from the holding temperature to RT. Each bulk sample has a relative density of 100%. The volume fractions of TiB_2 phases in B_4C - TiB_2 composites are determined by the equation (3).

$$\frac{V_{TiB_2}}{V_t} = \frac{\frac{m_{TiB_2}}{\rho_{TiB_2}}}{\frac{m_t}{\rho_t}} = w_{TiB_2} \cdot \frac{\rho_t}{\rho_{TiB_2}} \quad (3)$$

Where V_{TiB_2} and V_t are the volume of TiB_2 phases and the B_4C-TiB_2 composites, respectively. w_{TiB_2} is the weight percent of TiB_2 measured by using XRD, the calculated weight percent of TiB_2 for S1, S2 and S3 are 18 %, 26% and 44%, respectively. ρ_{TiB_2} (4.5 g/cm^3) is the density of TiB_2 and ρ_t is the density of the B_4C-TiB_2 composites (2.637, 2.796 and 3.051 g/cm^3 for S1, S2 and S3, respectively). The density of the B_4C-TiB_2 composites were measured by and Archimedes method. The chemical composition and the calculated volume fraction of each sample are shown in Table 1.

2.2. Vickers indentation tests and irradiation procedure

A pyramidal diamond tip with an apical angle of 136° was used to perform Vickers indentation tests. The tests were performed on the surface of the virgin samples to investigate the crack propagation behavior in the composite. During the indentation tests, the maximal load was set to 9.8 N, and the holding time was 15 s. Each indentation was set more than $100 \mu\text{m}$ apart to avoid an overlap of the indentation-induced deformations or crack outspread regions.

The He ion irradiation procedure was conducted in a terminal chamber with a 320 kV multidiscipline research platform for highly

charged ions at the Institute of Modern Physics (IMP), Lanzhou, China. Samples S1, S2, and S3 were irradiated with 500 keV He ions with 1×10^{17} ions/cm² at 773 K. After the irradiation process, the samples were annealed at 1273 K for 25 min in a vacuum of 10^{-5} Pa. In addition, Stopping Range of Ions in Matter (SRIM) codes were conducted with the Kinchin–Pease quick-calculation mode to predict the distribution of the He atoms and displacement damage in B₄C and TiB₂, respectively. The calculated distribution is a function of the penetration depth, as shown in Fig. 1; the Bragg peak with a He concentration of 8.92×10^{21} cm⁻³ (7.02%) is located at a depth of ~ 1.38 μ m in the B₄C material, and 7.18×10^{21} cm⁻³ (6.14%) at a depth of ~ 1.56 μ m in TiB₂ material, respectively.

2.3. Characterization

The morphology of the sample surface and Vickers indentation impression were recorded by scanning electron microscopy (SEM, Thermo Fisher Quanta FEG 250). In addition, the focused ion beam technology (Thermo Fisher, Helios G4 CX) was employed to lift up thin foils for the transmission electron microscopy (TEM) analysis. The thin foils were analyzed with a Talos F200X TEM at 200 kV in the bright-field mode, and a HV-1000 indentation test machine (Shanghai Lianer Testing Equipment Corporation) was used to perform the Vickers indentation tests.

3. Results and discussions

Before the SEM analysis, the composites were mechanically polished with diamond papers (from 800 to 12500 grit) until mirror-like surfaces were obtained. Fig. 2 shows the typical SEM images of the B_4C - TiB_2 composites with TiB_2 volume fractions of 10.5% (Fig. 2(a)), 16.2% (Fig. 2(b)), and 29.8% (Fig. 2(c)). The white contrast indicated by black arrows in the SEM images are TiB_2 phases, and the left, dark contrast represents B_4C grains. The TiB_2 phases are distributed along the B_4C grain boundaries. With increasing TiB_2 phase volume fraction, the fraction of isolated TiB_2 particles decreases, and more and more TiB_2 phases along the grain boundaries become connected, which results in an interconnected network from the two-dimensional (2D) point of view (Fig. 2(c)). Therefore, from the three-dimensional point of view, the TiB_2 network forms a cage-like structure, which encapsulates the B_4C matrix grains. The average thickness of the TiB_2 network of S3 is 0.9 μm , and the statistical measurement based on the line-intercept method [20] reveals that the mean grain sizes of B_4C in the S1, S2, and S3 samples are 9.5, 8.6, and 6.4 μm , respectively. Thus, the TiB_2 fraction increases at the expense of consumed B_4C .

To evaluate the effect of the TiB_2 network (cages) and its volume fraction on the heat transfer performance in the B_4C - TiB_2 composites, a series of numerical studies based on the typical microstructures of pure B_4C and B_4C - TiB_2 composites were implemented in the FE program

ABAQUS. The geometric constructions of the 2D pure B_4C and B_4C - TiB_2 composites FE model is shown in Fig. 3. A thermal continuity constraint was defined at each interface to connect the B_4C and TiB_2 domains without heat dissipation. An initial temperature of 773 K was assigned to the entire computational region to simulate the reactor environment temperature, and 1273 K (boundary condition) was assigned to the left end of each model to generate a stable heater source; the other boundary conditions were adiabatic boundary conditions. The temperature dependence of the physical parameters of B_4C and TiB_2 used in the numerical calculation are listed in Table 2 [18,21].

The temperature distributions used with different time scales for the pure B_4C and B_4C - TiB_2 composites models are shown in Fig. 4. The temperature distribution in pure B_4C is homogeneous along the vertical direction, and the isotherms are perpendicular to the horizontal axis. Whereas the temperature in the B_4C - TiB_2 composites presents an irregular gradient distribution. Furthermore, the temperature gradient in the B_4C - TiB_2 composites with a high TiB_2 volume fraction is lower than that of the low TiB_2 volume fraction. Particularly, the maximum temperature gradient appears in pure B_4C . Thus, heat is transmitted faster in the B_4C - TiB_2 composite than in the pure B_4C , the higher the volume fraction of TiB_2 , the faster the heat transfers, which is consistent with the experimental results in [19].

To compare the heat transfer performance of the four structures quantitatively, the temperature variations at the middle point of the right-end boundary in each model are presented with respect to time in Fig. 5. The heating rate in the B_4C - TiB_2 composite with higher TiB_2 volume fraction is higher than that of lower ones. For example, the temperature at point P_3 in the B_4C - TiB_2 composite with the highest TiB_2 volume fraction (29.8%) reaches 1181 K within 1 μs , while the temperature at point P_0 in the pure B_4C becomes only 1076 K within the same time. The FE analysis results demonstrate that the lower temperature gradient caused by the faster heat propagation in the B_4C - TiB_2 composites can be ascribed to the existence of the TiB_2 network in the B_4C matrix, which has a higher thermal conductivity. If the composites are used as neutron-absorbing pellets in nuclear reactors, their high thermal conductance can rapidly cool the local high temperature caused by the nuclear reactions and greatly reduce the thermal stress caused by the thermal gradient, which reduces the risk of structural failure.

To further determine the equivalent average parameters and average heat conducting characteristics of the B_4C - TiB_2 composite, the equivalent homogeneous models with all the homogenized model parameters, such as conductivity, specific heat and density, determined by the volume-weighted-average were implemented for the three cases of

different TiB_2 volume fractions (10.5%, 16.2% and 29.8%). Taking the temperature of the middle point of the right-end boundary as the assessment during simulation from 0.2 to 1 μs , the comparison of the results calculated from real composite structure and equivalent homogeneous models are summarized in Table 3. It can be seen that the results of the equivalent homogeneous models are slightly overestimated for the three cases, but the maximum relative error is less than 5%, which indicates that the simple volume-weighted-average method can be used to roughly predict the equivalent parameters and average heat conducting characteristics of the B_4C – TiB_2 composite for variational volume fraction. It demonstrates the expected conductivity enhancement brought by the interconnectivity of the TiB_2 phases as well.

In real nuclear reactors, the thermal gradient and He swelling-induced crack propagation in B_4C materials are mainly responsible for the disintegration of B_4C pellets in fast neutron reactors and in thermal neutron reactors, respectively. To investigate the effect of the TiB_2 network (cages) on the crack propagation behavior in the B_4C – TiB_2 composites, Vickers indentation was employed to simulate the external stress that was applied to the B_4C – TiB_2 composites.

The typical Vickers indentation marks on the surfaces of S1, S2, and S3 are shown in Figs. 6(a), (b), and (c), respectively. The beginnings and endings of the cracks are indicated by double-headed arrows. Note that in

the Fig. 6(c), the gradient of sunken area is steep, outline of the Vickers indentation impression is irregular, but four cracks of the indentation are obvious. Therefore, each crack length is measured from the end of the crack, and along the inverse direction of crack propagation to the point where crack origins from the steeply sunken area (i.e. the indentation impression area). At a load of 9.8 N, the length of the cracks on S1 range from 20.7 to 27.9 μm ; those on S2 and S3 range from 12.8 to 20.3 μm and 6.8 to 13.5 μm , respectively. The statistical results of the cracks show that the average values are 22.9 ± 2.8 , 16.1 ± 4.3 , and 12.2 ± 3.8 μm for S1, S2, and S3, respectively. Fig. 7 presents the statistical results of the crack lengths on S1, S2, and S3, respectively. Evidently, the crack lengths decrease with increasing TiB_2 volume fraction. Thereby the statistical results prove that the TiB_2 phase distribution along the grain boundaries can impinge/block the crack propagation.

Figs. 8(a) and (b) present the enlarged SEM images of the crack propagation paths in S1 and S3, respectively. The white contrast in Figs. 8(a) and (b) are TiB_2 phases: the TiB_2 phases in Fig. 8(a) are isolated particles, which are distributed in the B_4C matrix; the TiB_2 phases in Fig. 8(b) are interconnected, thereby forming a network (cages). The solid arrow in Fig. 8(a) indicates clearly that the propagating crack departs from its original straight trajectory and curves along the $\text{B}_4\text{C}/\text{TiB}_2$ interface, thereby proving that the isolated TiB_2 islands in the B_4C matrix

can redirect the crack propagation. A similar phenomenon was reported in [22]. In this study, the network (cages) topography in Fig. 8(b) clearly shows that the crack propagates through the TiB_2 walls (dashed arrows 2 and 3) and extends along the interface between the B_4C and TiB_2 phases (dashed arrow 1), which facilitates the energy release of the crack tip. This is confirmed by the shorter crack length ($12.2 \pm 3.8 \mu\text{m}$) of S3 than those of S1 ($22.9 \pm 2.8 \mu\text{m}$) and S2 ($16.1 \pm 4.3 \mu\text{m}$), as shown in Fig. 6.

It can be concluded that there are two underlying ways in which the TiB_2 phases affect the crack propagation in B_4C – TiB_2 composites: first, when the volume fraction of the TiB_2 phase is low, TiB_2 distributes in the B_4C matrix as isolated particles (shown in Fig. 8(a)), and when the propagation of a crack tip encounters a TiB_2 particle, the crack moves along the $\text{B}_4\text{C}/\text{TiB}_2$ interface, prolongs the crack propagation length and dissipates more energy, finally results in an improvement of the fracture toughness of the B_4C – TiB_2 composites. Similar dissipation mechanisms at the $\text{B}_4\text{C}/\text{TiB}_2$ interfaces are also found in Refs. [23, 24]. Second, when the volume fraction of the TiB_2 phase is high, the TiB_2 phase forms an enclosed cage-like structure that encapsulates the B_4C grains (Fig. 8(b)). Thus, the cracks have to penetrate the TiB_2 walls before extending along the $\text{B}_4\text{C}/\text{TiB}_2$ interfaces or must propagate through the neighboring B_4C grains. According to the model of Cook et al. on crack propagation in brittle systems [25], additional energy is required to deflect the crack

propagation and initiate secondary crack propagation across the interface;
the primary crack requires much energy.

To quantitatively measure the fracture toughness of the B₄C-TiB₂ composites, following equations are used [26]:

$$K_{IC} = 0.016(E/H_V)^{0.5}Pc^{-1.5}, \quad (4)$$

where

$$H_V = \frac{1.8544 \times P}{4a^2 \times 1000}, \quad (5)$$

in which E is the Young's modulus, H_V the Vickers hardness, P the Vickers indentation load, and a and c are the half length of the residual Vickers indenter impression diagonal and half length of the radial crack diagonal, respectively. The fracture toughness of the composites K_{IC} were calculated to be 3.06 ± 0.28 (MPa·m^{1/2}), 3.81 ± 0.33 (MPa·m^{1/2}), and 4.38 ± 0.67 (MPa·m^{1/2}) for S1, S2, and S3, respectively. In other words, increasing the TiB₂ volume fraction and optimizing the distribution of TiB₂ can impinge/block the propagation of cracks and improve the fracture toughness of the B₄C-TiB₂ composites. This promotes the integration of B₄C pellets and improves the CR performance in the harsh environments of nuclear reactors.

He behavior of the composites under irradiation conditions is important for the evaluation of the composites serving in the reactors, however, it was seldomly studied. Therefore, we conducted He ions irradiation on the composites and initially investigated the He behavior by

TEM observation.

The TEM images in Fig. 9 show the He bubble distribution and morphology in B₄C phase of samples S1, S2, and S3. The images were recorded with the same underfocus of 2.8 μm . The He bubbles, which are small bright dots in the images, are located within a band area. The width of He bubbles deposition band is smaller than that of the implanted band as calculated by SRIM, similar phenomenon is observed by Motte et al. [8]. It is suggested that this is due to the different depths of the He ions induced damage profile and the He ions implanted profile. In the area of the damage profile, lot of vacancies were introduced by energetic ions collision, while in the area of He atoms implanted band, He atoms greatly outnumbered the vacancies. In the overlapped areas (the width of which was smaller than the implanted band as calculated by SRIM), abundant vacancies and He atoms promoted the formation of He-vacancy clusters and increased the density of He bubble germs. After annealing, He-vacancy clusters evolved into visible He bubbles under TEM observation and formed a bubbles band in the overlapped area. Moreover, Gillet et al. found that the dissociation energy of He-vacancy is ~ 2 eV, the high energy barrier inhibited the He diffusion by the formation of He-vacancy clusters [27], and this explained that no He bubbles outside the band area can be found (excepted the He bubbles in the grain boundaries).

The He bubbles in the bubbles band are small and dense; such feature has been argued to arise partially from the diffusion behavior of He atoms in B_4C . According to Refs. [27-30], He atoms must overcome a high energy barrier to migrate even through the most probable migration paths owing to the intrinsic chemical bond and lattice structure of B_4C . Schneider et al. discovered that He atoms prefer to migrate between $\langle 111 \rangle$ planes by first-principle calculations. Moreover, they discovered that the activation energy of He ion diffusion is approximately 2 eV [28], which is consistent with the experimental results in [30]. The 2 eV migration energy means that the aggregation of He atoms in B_4C materials is retarded and explains the observation of small-sized He bubbles in this study rather than large-sized He bubbles in metals under similar irradiation conditions [31].

The He bubbles that are distributed along the interfaces are bigger than the bubbles distributed in the B_4C and TiB_2 grains (however, bubbles along the TiB_2 – TiB_2 interface are not investigated in this study), as shown in Fig. 10. This is due to the special structure of the interface. Misfits in the lattice structure of the interfaces contain plenty of open volume [32], which provides adequate free space for the deposition of irradiation-induced point defects (e.g., vacancies, interstitials, transmuted elemental atoms) [33]. Owing to the high binding energy between vacancies and He atoms (~ 2 eV [27,28]), the open volume of interfaces

can act as efficient trapping sites for He and preferential nucleation sites for He bubbles [8,9,34]. Therefore, once the He atoms are captured by the interfaces, they cannot easily be released within the temperature range investigated in this study. As shown in Fig. 10, no He bubbles depleted zone was detected, which is consistent with the results of Motte et al.'s work [28] that it was hard for He atoms to diffuse through or in the B_4C grain boundaries below 1373 K. This might prove that long-range He diffusion is negligible at 1273 K. Moreover, TEM image in Fig. 10 shows that He bubbles deposition band in B_4C is closer to the surface than that in TiB_2 , this phenomenon is also consistent with SRIM calculation as shown in Fig. 1 that the overlap of He distribution and damage profile is shallower in B_4C than that in TiB_2 .

In a realistic environment of nuclear reactors, increasing the density of sinks for the precipitation of He atoms is an effective way to suppress the formation of large He bubbles [35], and reduce the He-induced property degradation (e.g. He embrittlement). Therefore, the network (cages) of the TiB_2 phases provides numerous sinks for He precipitation, which might inhibit the formation of large He bubbles, and mitigate the effects of He-accumulation-induced shear stress at interfaces, and the resulting microcracks, especially in the thermal neutron reactors. However, other factors may affect performance of the B_4C - TiB_2 composites, such as shear stress induced by He accumulation at the

419 interfaces, different thermal dilation between B_4C and TiB_2 . To have a
420 better evaluation of the B_4C – TiB_2 composites in a realistic environment, a
421 detailed numerical evaluation will be carried out in the future study.

422 As an important component of the B_4C –diborides composites, the
423 behavior of diborides under irradiation environment is very crucial to the
424 performance of composites. Cheminant et al. conducted neutron
425 irradiation on HfB_2 , and found that porosity appeared at grain boundaries,
426 and resulted in a decrease of the thermal diffusivity [36], which lead to
427 the degradation of B_4C – HfB_2 composites. Regarding the TiB_2 in this
428 study, despite the inimitable merits of TiB_2 , however, its irradiation
429 behavior was seldomly studied, which is very important for the
430 application of TiB_2 as neutron absorbers. To the best of our knowledge,
431 only two studies reported the microstructural evolution of TiB_2 under
432 irradiation conditions [37, 38]. Therefore, a systematic study on the
433 irradiation tolerance of TiB_2 is needed, which will be part of our future
434 work.

435 3. Conclusion

436 To improve the performance of B_4C neutron absorption material in
437 nuclear reactors, a set of property-optimized B_4C – TiB_2 composites were
438 designed and fabricated through a combination of the molten-salt and
439 SPS methods. The TiB_2 phase distributes along the B_4C grain boundaries
440 and forms a connected network (cages), which encapsulates the B_4C

matrix phase. The thermal conductivity and fracture toughness of the B_4C - TiB_2 composites are greatly improved owing to the special cage-like structure. The FE analyses show that the connected TiB_2 network promotes the heat transfer and improves effectively the overall thermal conductivity of the B_4C - TiB_2 composite. The improved thermal conductivity results in a lower thermal stress, which mitigates thermal-stress-induced crack propagation.

Vickers indentation tests were performed on the composites to study the crack propagation behavior. The TiB_2 network (cages) can effectively impinge/block the crack propagation, thereby improving the composite fracture toughness. This is important for maintaining the integration of B_4C - TiB_2 composites if the composite serves as neutron absorption material in nuclear reactors.

Moreover, He ion irradiation was used to investigate the He behavior in the composites and to simulate the situation in which a high quantity of He is produced by the $B^{10}(n, \alpha) Li^7$ nuclear reaction. The TEM results show that the interfaces of B_4C and TiB_2 are effective trapping sites for He atoms and nucleation sites for He bubbles. Note that in a fast neutron reactor, the ballistic damage induced by energetic neutrons scattering and the nuclear reaction products (e.g., He, Li) scattering are much higher than the sole He ions implantation, this leads to a higher vacancy/He ratio and the possible consequences on the defects dynamics [28].

Overall, this study provides a synthesis method for fabricating neutron absorption materials for the application in nuclear reactors. The special property-optimized B_4C - TiB_2 composites with designed microstructure exhibit a better resistance to disintegration under irradiation and in the thermodynamic environment of nuclear reactors. In addition, they have a great potential for the application as neutron-absorbing pellets in nuclear reactors.

In the future study, other issues will be addressed to have a comprehensive evaluation of B_4C - TiB_2 composites under irradiation conditions. For example, helium behavior in TiB_2 and irradiation resistant property of TiB_2 , effects of the special cage-like structure and TiB_2 content on He diffusion and release during annealing, other synthesis routes to optimize the structure and properties of the B_4C - TiB_2 composites, influence of He bubbles aggregation along the B_4C - TiB_2 and TiB_2 - TiB_2 interface on the thermal conductivity of the composites and the crack propagation behavior, etc.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 11902129, 11805245), Strategic Priority Research Program of Chinese Academy of Sciences (No. XDA21010202), Natural Science Fund of Zhejiang Province (No. LQ20A050001), Natural Science Fund of Ningbo City (No. 2019A610183), and China

485 Postdoctoral Science Foundation (2019T120963).

486 Data availability

487 The raw data required to reproduce these findings cannot be shared at
488 this time as the data is part of an ongoing study. The processed data
489 required to reproduce these findings cannot be shared at this time as the
490 data is part of an ongoing study.

491 References

492 [1] T. Donomae, K. Maeda, Fast Spectrum Control Rod Materials, in:
493 R.J.M. Konings, T.R. Allen, R.E. Stoller, S. Yamanaka (Eds.),
494 Comprehensive nuclear materials, Elsevier, Netherlands, 2012, pp.
495 509-534.

496 [2] T. Maruyama, S. Onose, T. Kaito, H. Horiuchi, J. Nucl. Sci. Technol.
497 34 (10) (1997) 1006-1014.

498 [3] N. Moncoffre, N. Toulhoat, N. Bererd, Y. Pipon, G. Silbermann, A.
499 Blondel, N. Galy, P. Sainsot, J.-N. Rouzaud, D. Deldicque, V. Dauvois, J.
500 Nucl. Mater. 472 (2016) 252-258.

501 [4] V. Kerleguer, C. Jegou, L. D. Windt, V. Broudic, G. Jouan, S. Miro, F.
502 Tocino, C. Martin, J. Nucl. Mater. 529 (2020) 151920.

503 [5] D. Gosset, Absorber materials for generation IV reactors, in: P. Yvon,
504 Structural Material for Generation IV Nuclear reactors, Elsevier,
505 Netherlands, 2017, pp. 533-567.

506 [6] IAEA-TECDOC-1132, Control Assembly Materials for Water

- 507 Reactors: Experience, Performance and Perspectives, 1998.
- 508 [7] G.W. Hollenberg, J.A. Basmajian, J. Am. Ceram. Soc. 65 (4) (1982)
- 509 179-181.
- 510 [8] V. Motte, D. Gosset, G. Gutierrez, S. Doriot, N. Moncoffre, J. Nucl.
- 511 Mater. 514 (2019) 334-347.
- 512 [9] T. Stoto, J. Ardonceau, L. Zuppiroli, M. Castiglioni, B. Weckermann,
- 513 Radiat. Eff., 105 (1987) 17-30.
- 514 [10] R. M. Horn, B. D. Frew, P. V. Diemen, Thermal Spectrum Control
- 515 Rod Materials, in: R.J.M. Konings, T.R. Allen, R.E. Stoller, S. Yamanaka
- 516 (Eds.), Comprehensive nuclear materials, Elsevier, Netherlands, 2012, pp.
- 517 485-507.
- 518 [11] D. Gosset, M. Colin, Tech. Ing. BN3720 (2007).
- 519 [12] G.M. Decroix, D. Gosset, B. Kryger, M. Boussuge, H. Burlet,
- 520 Improvement of thermomechanical properties of ceramic materials for
- 521 nuclear applications, in: P. Vincenzini (Ed.), 8th CIMTEC, Florence, Italy,
- 522 1994.
- 523 [13] K. Sairam, J.K. Sonber, T.S.R.Ch. Murthy, C. Subramanian, R.C.
- 524 Hubli, A.K. Suri, Int. J. Ref. Met. Hard Mater. 35 (2012) 32-40.
- 525 [14] J. Matsushita, T. Suzuki, A. Sano, J. Ceram. Soc. Jpn. 101 (9) (1993)
- 526 1074-1077.
- 527 [15] B. Basu, G.B. Raju, A.K. Suri, Int. Mater. Rev. 51 (6) (2006) 352-
- 528 374.

- 529 [16] Z.H. Zhang, X.B. Shen, F.C. Wang, S.K. Lee, Q.B. Fan, M.S. Cao,
530 Scr. Mater. 66 (3–4) (2012) 167–170.
- 531 [17] C. Subramanian, T.S.R.C. Murthy, A.K. Suri, Int. J. Refract. Met.
532 Hard Mater. 25 (4) (2007) 345–350.
- 533 [18] R.G. Munro, J. Res. Natl. Inst. Stand. Technol. 105(2000)709-720.
- 534 [19] D.L. Ren, Q. Deng, J. Wang, J.S. Yang, Y.B. Li, J.Q. Shao, M. Li, J.
535 Zhou, S.L. Ran, S.Y. Du, Q. Huang, J. Am. Ceram. Soc. 101 (2018) 1–7.
- 536 [20] J.C. Wurst, J.A. Nelson, J. Am. Ceram. Soc. 55 (2) (1972) 109.
- 537 [21] P.A. Medwick, H.E. Fischer, R.O. Pohl, J. All. Comp. 203 (1994)
538 67-75.
- 539 [22] S. Yamada, K. Hirao, Y. Yamauchi, S. Kanzaki, J. Eur. Ceram. Soc.
540 23 (2003) 1123-1130.
- 541 [23] Y. Zhu, H.W. Cheng, Y.W. Wang, R. An, J. All. Comp. 772 (2019)
542 537-545.
- 543 [24] M.S. Heydari, H.R. Baharvandi, K. Dolatkhah, Int. J. Refract. Met.
544 Hard Mater. 51 (2015) 6-13.
- 545 [25] J. Cook, J. E. Gordon, C. C. Evans, D. M. Marsh, Proc. R. Soc. Lond.
546 A 282(1964)508-520.
- 547 [26] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, J. Am. Ceram.
548 Soc. 64 (1981) 533-538.
- 549 [27] K. Gillet, G. Roma, J.P. Crocombette, D. Gosset, J. Nucl. Mater. 512
550 (2018) 288-296.

- 551 [28] V. Motte, D. Gosset, T. Sauvage, H. Lecoq, N. Moncoffre, J. Nucl.
552 Mater. 517 (2019) 165-174.
- 553 [29] A. Schneider, G. Roma, J.P. Crocombette, V. Motte, D. Gosset, J.
554 Nucl. Mater. 498 (2017) 157-162.
- 555 [30] D. Horlait, D. Gosset, A. Jankowiak, V. Motte, N. Lochet, T. Sauvage,
556 E. Gilabert, J. Nucl. Mater. 527(2019)151834.
- 557 [31] M.H. Cui, J. Wang, Z.G. Wang, T.L. Shen, K.F. Wei, C.F. Yao, J.R.
558 Sun, N. Gao, Y.B. Zhu, L.L. Pang, D. Wang, H.P. Zhu, Y. Han, X.S. Fang,
559 Nucl. Instrum. Methods Phys. Res., Sect. B 406 (2017) 611-617.
- 560 [32] Ilya A. Ovid'ko, Rev. Adv. Mater. Sci. 1 (2000) 61-107.
- 561 [33] I.J. Beyerlein, A. Caro, M.J. Demkowicz, N.A. Mara, A. Misra, B.P.
562 Uberuaga, Mater. Today 16 (2013) 443-449.
- 563 [34] D. Gosset, P. Herter, V. Motte, Nucl. Instrum. Methods Phys. Res.,
564 Sect. B 434 (2018) 66-72.
- 565 [35] P.D. Edmondson C.M. Parish, Y. Zhang, A. Hallen, M.K. Miller,
566 Scripta Mater. 65 (2011) 731-734.
- 567 [36] P. Cheminant, X. Deschanel, L. Boulanger, A. Thorel, Key Eng.
568 Mater. 132-136 (1997) 643-646.
- 569 [37] M. Carrard, D. Emin, L. Zuppiroli, Phys. Rev. B 51 (1995)
570 11270-11274.
- 571 [38] A. Bhattacharya, C.M. Parish, T. Koyanagi, C.M. Petrie, D. King, G.
572 Hilmas, W.G. Fahrenholtz, S.J. Zinkle, Y. Katoh, Acta Mater. 165 (2019)

573 26-39.

574

575 Figure captions

576 Fig. 1. Displacement damage and He concentration as a function of
577 penetration depth in B_4C and TiB_2 material, respectively.

578 Fig. 2. SEM images of surface morphology of (a) 10.5 Vol.% TiB_2
579 composites, (b) 16.2 Vol.% TiB_2 composites, and (c) 29.8 Vol.% TiB_2
580 composites; arrows indicate the TiB_2 phases.

581 Fig. 3. Geometric construction and boundary conditions of FE models: (a)
582 pure B_4C model; (b)-(d) B_4C - TiB_2 composite model based on SEM
583 image of sample S1, S2 and S3, respectively; light and dark contrasts
584 represent TiB_2 network and B_4C matrix, respectively; P_i ($i=0, 1, 2$ and 3)
585 represents middle point of the right-end boundary of each calculated
586 domain.

587 Fig. 4. Temperature distribution in pure B_4C and B_4C - TiB_2 composites
588 with different TiB_2 volume fractions at different time scales calculated by
589 FE method: (a) pure B_4C ; (b)-(d) B_4C - TiB_2 composites of sample S1, S2
590 and S3, respectively.

591 Fig. 5. Temperature variation at points P_i (center of the right-end
592 boundary in each model) with respect to time.

593 Fig. 6. Typical Vickers indentation impressions on (a) 10.5 Vol.% TiB_2
594 composites, (b) 16.2 Vol.% TiB_2 composites, and (c) 29.8 Vol.% TiB_2

composites. The double arrows indicate the starting to the ending of the cracks.

Fig. 7. Statistical results of Vickers indentation-induced crack length for different TiB_2 volume fractions of composites.

Fig. 8. SEM images of Vickers indentation-induced crack propagation; solid arrows in (a) indicate deflection of cracks by isolated TiB_2 particles, and dashed arrows in (b) indicate crack penetration through TiB_2 cages.

Fig. 9. TEM images of He bubble morphology in He deposition band in B_4C phase of (a) 10.5 Vol.% TiB_2 composites, (b) 16.2 Vol.% TiB_2 composites, and (c) 29.8 Vol.% TiB_2 composites.

Fig. 10. TEM image of He bubble morphology in He deposition band and at B_4C – TiB_2 interfaces. The arrows indicate the incident direction of He ions. The dash lines indicate the boundaries of He bubbles band.

Table 1. Molar ratio of raw B_4C powder and Ti powder for molten-salt reaction, volume fraction of TiB_2 , weight percent of TiB_2 , B_4C and C in synthesized bulks.

Samples	Molar ratio ($\text{B}_4\text{C}:\text{Ti}$)	Volume fraction of TiB_2	Weight percent of TiB_2	Weight percent of B_4C	Weight percent of C
S1	6:1	10.5%	18.0%	80.4%	1.6%
S2	4:1	16.2%	26.0%	72.0%	2.0%
S3	2:1	29.8%	44.0%	52.0%	4.0%

Table 2. Material properties of B_4C and TiB_2 used in heat transfer

613

analysis [16, 19]

Temperature (K)	Conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)		Specific Heat ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$)		Density (kg/m^3)	
	773	1273	773	1273	773	1273
B_4C	20.00	11.00	1680.80	2072.68	2550	2550
TiB_2	81.00	78.10	1073.00	1186.00	4450	4390

614

615 Table 3. Comparison of the results calculated from real composite
 616 structure models (CM), equivalent homogeneous models (HM) and the
 617 relative error (RE).

Time (μs)	S1			S2			S3		
	CM(K)	HM(K)	RE(%)	CM(K)	HM(K)	RE(%)	CM(K)	HM(K)	RE(%)
0.2	819	836	2.1	832	856	2.9	867	901	3.9
0.4	917	948	3.4	941	981	4.3	997	1043	4.6
0.6	996	1033	3.7	1024	1069	4.4	1093	1129	4.2
0.8	1057	1093	3.7	1085	1128	4.0	1142	1180	3.3
1	1102	1137	3.2	1130	1168	3.4	1181	1212	2.6

618

619

Fig. 1. Displacement damage and He concentration as a function of penetration depth in B_4C and TiB_2 material, respectively.

Fig. 2. SEM images of surface morphology of (a) 10.5 Vol.% TiB_2 composites, (b) 16.2 Vol.% TiB_2 composites, and (c) 29.8 Vol.% TiB_2 composites; arrows indicate the TiB_2 phases.

Fig. 3. Geometric construction and boundary conditions of FE models: (a) pure B_4C model; (b)-(d) B_4C - TiB_2 composite model based on SEM

image of sample S1, S2 and S3, respectively; light and dark contrasts represent TiB_2 network and B_4C matrix, respectively; P_i ($i=0, 1, 2$ and 3) represents middle point of the right-end boundary of each calculated domain.

Fig. 4. Temperature distribution in pure B_4C and $\text{B}_4\text{C-TiB}_2$ composites with different TiB_2 volume fractions at different time scales calculated by FE method: (a) pure B_4C ; (b)-(d) $\text{B}_4\text{C-TiB}_2$ composites of sample S1, S2 and S3, respectively.

Fig.5. Temperature variation at points P_i (center of the right-end boundary in each model) with respect to time.

Fig. 6. Typical Vickers indentation impressions on (a) 10.5 Vol.% TiB_2 composites, (b) 16.2 Vol.% TiB_2 composites, and (c) 29.8 Vol.% TiB_2 composites. The double arrows indicate the starting to the ending of the cracks.

Fig. 7. Statistical results of Vickers indentation-induced crack length for different TiB_2 volume fractions of composites.

Fig. 8. SEM images of Vickers indentation-induced crack propagation; solid arrows in (a) indicate deflection of cracks by isolated TiB_2 particles, and dashed arrows in (b) indicate crack penetration through TiB_2 cages.

Fig. 9. TEM images of He bubble morphology in He deposition band in B_4C phase of (a) 10.5 Vol.% TiB_2 composites, (b) 16.2 Vol.% TiB_2 composites, and (c) 29.8 Vol.% TiB_2 composites.

Fig. 10. TEM image of He bubble morphology in He deposition band and at B_4C - TiB_2 interfaces. The arrows indicate the incident direction of He ions. The dash lines indicate the boundaries of He bubbles band.

B_4C - TiB_2 composites with B_4C grains encapsulated by TiB_2 network (cages) are fabricated.

TiB_2 network (cages) greatly improve thermal conductivity and fracture toughness of B_4C - TiB_2 composites.

The interconnected interfaces between TiB_2 network (cages) and B_4C grains act as effective sinks for the aggregation of He atoms.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

--