

High-dose neutron irradiation of beryllium and titanium beryllide: Summary and outlook

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ABSTRACT

The irradiation experiment conducted in the HFR material testing reactor, under conditions simulating the operating environment of the DEMO breeding blanket, along with subsequent post-irradiation examinations (PIEs) of irradiated beryllium-based materials—such as pure beryllium and titanium beryllide—enabled a comparative analysis of their radiation resistance for potential use as neutron multipliers. The PIEs clearly demonstrated the superiority of titanium beryllide over beryllium, particularly in terms of reduced swelling, lower tritium retention, and enhanced mechanical properties at elevated temperatures. As a result, titanium beryllide blocks have been proposed to replace beryllium pebbles in the Helium-Cooled Pebble Bed (HCPB) DEMO breeding blanket design. A production technology for fabricating titanium beryllide blocks was successfully developed, and further advancements in this technology, along with research on full-scale blocks, have been outlined.

1. Introduction

The purpose of this article is to show the main results obtained during of post-irradiation examinations (PIEs) of Be-based materials from HIDOBE-01 and -02 capsules, and the consequences of the PIEs as a significant adjustment to the HCPB DEMO blanket concept.

In the 1990s, beryllium, with its unique nuclear properties, began to be considered as a potential neutron multiplier for ITER and DEMO [1,2]. The Helium-Cooled Pebble Bed (HCPB) concept for the DEMO blanket was proposed, featuring beryllium pebbles as the neutron multiplier [3,4]. However, early experimental results revealed significant challenges associated with neutron irradiation effects on beryllium, including high swelling and considerable tritium retention in helium bubbles formed within its microstructure during irradiation [5–7].

At the start of the 21st century, intermetallic compounds such as

beryllides—specifically titanium beryllide—were proposed as alternative neutron multipliers [8,9]. Initial studies demonstrated the potential advantages of titanium beryllide over pure beryllium as a neutron multiplier for the DEMO blanket [10–13]. Recognizing the need for further evaluation, the international fusion research community initiated an irradiation test to compare beryllium and titanium beryllide under conditions representative of the DEMO blanket's operating environment.

This test, conducted at the HFR reactor in Petten, Netherlands, began in 2005 [14]. It comprised two phases (HIDOBE-01 and HIDOBE-02 campaigns), which varied significantly in terms of damage dose and helium and tritium accumulation. Two irradiation capsules were exposed to helium levels of 3000 and 6000 appm within beryllium, corresponding to up to 30 % of the end-of-life helium production anticipated in the DEMO tritium breeding blanket. Four DEMO-relevant

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irradiation temperatures, ranging from 673 to 1073 K, were selected [14].

This paper aims to present the main findings from post-irradiation examinations (PIEs) of beryllium-based materials from the HIDOBE-01 and -02 campaigns and to discuss their implications for refining the HCPB DEMO blanket design.

2. Experimental

2.1. Materials, samples

This study utilized beryllium (Be) and titanium beryllide Be-7at.%Ti (Be7Ti) materials, prepared as pellets measuring $\varnothing 8 \times 2$ mm, produced through vacuum arc melting [9,14]. Additionally, beryllium pebbles with a diameter of 1 mm, manufactured using the Rotating Electrode Method (REM) by NGK, Japan, were included in the irradiation experiments during the HIDOBE-01 and -02 campaigns. The chemical compositions of the Be and Be7Ti materials are detailed in Table 1.

2.2. Irradiation

Beryllium and Be7Ti pellets, along with $\varnothing 1$ mm beryllium pebbles, were irradiated in the HIDOBE-01 and -02 capsules at the HFR in Petten, Netherlands, during 2005–2011 [14–16]. The irradiation parameters are presented in Tables 2 and 3. The damage dose calculations were performed according to the NRT standard for the placement of the samples in the reactor channels during irradiation.

2.3. Post-irradiation examinations (PIEs)

The post-irradiation examinations (PIEs) of Be-based materials irradiated in the HIDOBE-01 and -02 campaigns were conducted at the Karlsruhe Institute of Technology (KIT) in Germany and the Nuclear Research & Consultancy Group (NRG) in the Netherlands. These studies were carried out under the overall guidance and financial support of Fusion for Energy (F4E).

The swelling of the irradiated Be-based materials was assessed using immersion, dimensional, and helium pycnometry methods.

For Thermal-Programmed Desorption (TPD) tests, a quarter of a Be or Be7Ti pellet or several $\varnothing 1$ mm Be pebbles were utilized. The tests employed a flow-through setup equipped with a quadrupole mass spectrometer (QMS) and an ionization chamber (IC). The purge gas used was Ar + 0.1 vol% H₂. The temperature was ramped at heating rates of either 1 K/min (0.017 K/s) or 7 K/min (0.117 K/s) up to 1373 K, with a hold time of 3 h at the maximum temperature.

The Laser Flash method (Laser Flash Analyzer, LFA) was used to determine the thermal diffusivity of Be and Be7Ti pellets irradiated

Table 1

Chemical composition of Be and Be7Ti pellets and $\varnothing 1$ mm Be pebbles in wt.%.

Element/Oxide	Be pellet	Be pebble	Be7Ti
Be	99.5	99.5	71.2
O	0.0128	0.2304	0.1728
Ti			28.5
V			<0.01
W			<0.05
Mg	0.05	0.024	<0.001
Al	0.07	0.048	0.06
Si	0.03	0.029	0.033
Cr	<0.01		0.005
Fe	0.1	0.094	0.031
Co	0.0003	<0.001	<0.001
Ni	0.01		0.003
Cu	<0.01		0.004
Mn	0.007		0.007
Sc		<0.005	<0.001
U	0.0068	<0.01	0.0041

Table 2

Irradiation parameters of Be and Be7Ti materials in HIDOBE-01 rig (Be and Be7Ti pellets/Be pebbles).

T _{irr} , K	F, $\times 10^{26}$ m ⁻² , E > 1 MeV	D, dpa	⁴ He, appm	³ H, appm
696/640	0.73/0.57	15/11	2370/1890	215/176
783/700	0.88/0.69	18/14	2860/2300	279/213
930/800	0.94/0.81	19/16	3070/2680	305/252
1005/910	0.93/0.89	19/18	3060/2950	301/285

Table 3

Irradiation parameters of Be and Be7Ti materials in HIDOBE-02 rig (Be and Be7Ti pellets/Be pebbles).

T _{irr} , K	F, $\times 10^{26}$ m ⁻² , E > 1 MeV	D, dpa	⁴ He, appm	³ H, appm
710/643	1.16/1.06	23/21	4144/3632	430/367
800/723	1.51/1.43	31/29	5142/4751	550/502
940/833	1.73/1.68	36/34	5757/5524	625/596
1040/923	1.82/1.81	38/37	5992/5925	653/644

during the HIDOBE-02 experiment. These LFA measurements were conducted using the Netzsch LFA 457 system in the NRG hot cell laboratory. The data obtained from the LFA tests were used to calculate the thermal conductivity λ (W/(m·K)) using the following relation [17]:

$$\lambda = \alpha \cdot \rho \cdot c_p, \quad (1)$$

where α is the thermal diffusivity, m²/s; ρ is the density, kg/m³; c_p is the specific heat, J/(kg·K).

The optical microscopy (OM) study was performed by Olympus GX51 Light Optical Microscope which is with remote control and located in a hot cell. Bright field and dark field conditions can be applied as contrasting techniques as well as polarized light methods.

For irradiated Be-based samples, Vickers hardness HV0.4 tests were performed by the diamond pyramid with a loading velocity of 0.2 N/s reaching the maximum loading of 4 N to the total time of 10 s. For irradiated TiBe₁₂ samples, Vickers hardness HV0.1 tests were performed by the same diamond pyramid with the same loading velocity of 0.2 N/s reaching the maximum loading of 1 N to 10 s.

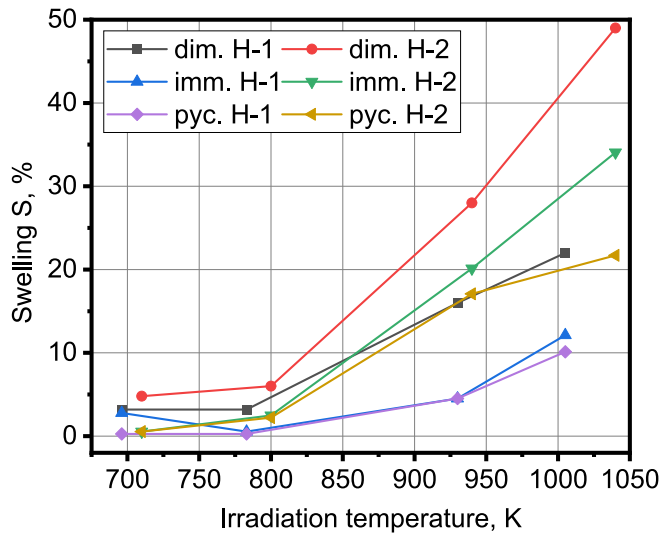
The TEM studies were performed using an FEI Tecnai 20 FEG microscope with an accelerating voltage of 200 kV, equipped with a scanning unit that allows scanning TEM (STEM) with a HAADF (High-Angle-Annular Dark Field) detector and an EDX (Energy Dispersive X-ray) detector for elemental analysis, as well as EELS (Electron Energy Loss Spectroscopy) spectroscopy for the detection of light elements such as Be or O. The imaging of defects was performed using bright field (BF) imaging.

The nanoscale of the materials was investigated using a Thermo-fisher Talos F200X scanning transmission electron microscope (STEM) equipped with a SuperX energy-dispersive X-ray detection system as well as with a Gatan Enfinium electron energy-loss spectroscope. The microscope was operated at 200 kV acceleration voltage.

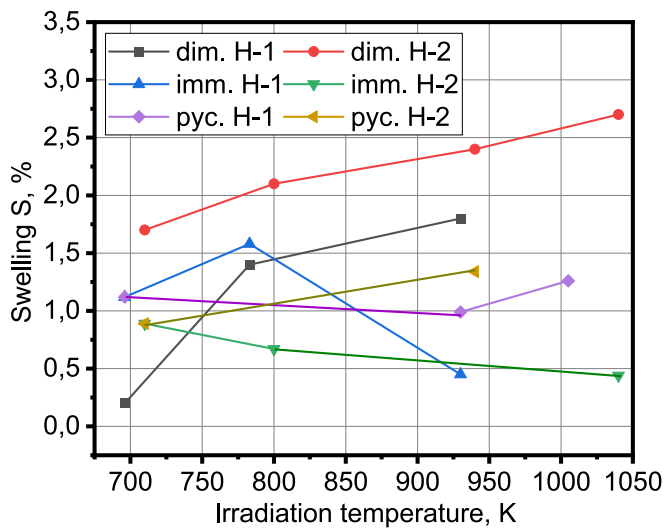
3. Results

3.1. Swelling

Fig. 1a illustrates the relationship between swelling (S) of the cast beryllium pellets and increasing irradiation temperature during the HIDOBE-01 and -02 campaigns. Swelling was determined using dimension measurements as well as immersion and pycnometry techniques. Up to an irradiation temperature of 800 K, swelling remains below 5 %. However, as the temperature rises to 1040 K, the swelling increases dramatically, reaching 50 % by use of the dimension method for samples irradiated at 800 K in HIDOBE-02. The other two methods (immersion and helium pycnometry) give swelling values from 20 to 35 %.



a



b

Fig. 1. Swelling S of Be and Be7Ti versus irradiation temperature (dim.– dimension, imm.– immersion, pyc.– pycnometry, H-1– HIDOBE-01, H-2– HIDOBE-02): $F = (0.73\text{--}1.82) \cdot 10^{22} \text{ cm}^{-2}$ ($E > 1 \text{ MeV}$) for Be, $F = (0.73\text{--}1.82) \cdot 10^{22} \text{ cm}^{-2}$ ($E > 1 \text{ MeV}$) for Be7Ti.

Fig. 1b depicts the swelling (S) of Be7Ti pellets in relation to irradiation temperature. The maximum swelling observed, measured by the dimension method for the HIDOBE-02 samples, is 2.7 % at the highest irradiation temperature of 1040 K. The HIDOBE-02 samples measured by the dimension method exhibit a relatively higher swelling compared to other methods (immersion and pycnometry). The swelling values in this case remain below 1.8 % having an irregular behavior at different irradiation temperatures.

The obtained results clearly demonstrate that the swelling of titanium beryllide Be7Ti is significantly lower than that of pure beryllium under comparable irradiation conditions [18].

3.2. Tritium release and retention

Fig. 2 presents tritium release spectra for Be (Fig. 2a) and Be7Ti (Fig. 2b) pellets irradiated at 783 K in the HIDOBE-01 campaign, both

characterized by a single sharp release peak. Similar spectra were observed for both Be and Be7Ti pellets irradiated in the HIDOBE-01 and -02 campaigns at different temperatures [15,16].

Fig. 3 illustrates the tritium content in Be and Be7Ti samples as determined from TPD tests, revealing a marked difference in how irradiation affects tritium behavior in these materials. Specifically, Be7Ti exhibits significantly lower tritium retention compared to Be (see Fig. 4).

When comparing experimental results with calculated values, a notable discrepancy is observed: the calculated tritium content generally exceeds the experimental values, except at 710 K and 800 K for Be, where the experimental results surpass the calculated ones (see Fig. 3). This anomaly may stem from uncertainties in neutron flux distribution along the reactor core height during the prolonged irradiation in HIDOBE-02, leading to deviations in the tritium content calculations for the samples. Despite this inconsistency, the key finding remains clear: Be7Ti retains substantially less tritium than Be under comparable conditions (see Fig. 4) [16,17,20–22].

3.3. Thermal conductivity

Fig. 5 shows the thermal conductivity of Be and Be7Ti before and after irradiation in the HIDOBE-02 with increasing testing temperature. The thermal conductivity values were calculated for each material for testing temperatures T_{test} equal to the irradiation temperatures T_{irr} using relation (1). After irradiation at two maximum temperatures of 940 and 1040 K, the thermal conductivity of Be samples sharply decreases on increasing testing temperature relative to the unirradiated state. However, the Be7Ti samples reveal a slight, almost constant decrease regardless of the irradiation temperature. Thus, after irradiation at two highest temperatures, the thermal conductivity of Be and Be7Ti samples approaches as follows: 60–65 W/(m K) is for Be and 36 W/(m K) is for Be7Ti.

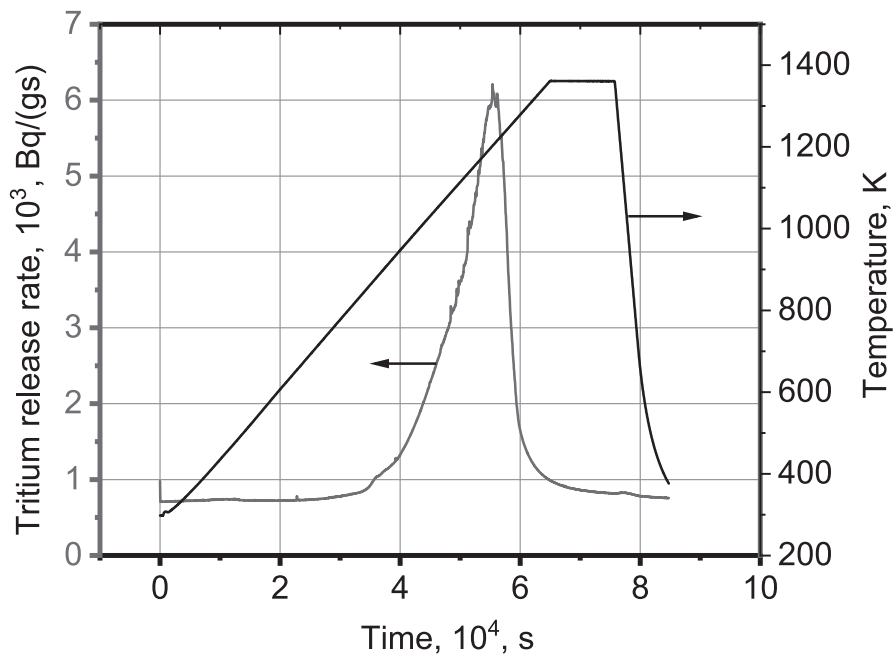
Fig. 5 displays the thermal conductivity of Be and Be7Ti both before and after irradiation in HIDOBE-02 as a function of increasing testing temperature. Thermal conductivity values were determined for each material at testing temperatures T_{test} matching their irradiation temperatures T_{irr} as calculated using relation (1). Following irradiation at the highest temperatures of 940 K and 1040 K, the thermal conductivity of Be exhibits a sharp decline with increasing testing temperature compared to its unirradiated state. In contrast, the Be7Ti samples show a relatively small and nearly consistent reduction in thermal conductivity, independent of the irradiation temperature.

Consequently, after irradiation at these maximum temperatures, the thermal conductivity stabilizes at approximately 60–65 W/(m K) for Be and 36 W/(m K) for Be7Ti. The two-phase structure of Be7Ti (comprising TiBe12 and Be phases) remains stable under high-dose neutron irradiation across all temperatures, with the Be-phase content unaffected by irradiation temperature. This stability aligns with the observed consistency in thermal conductivity across the irradiation temperature range [24].

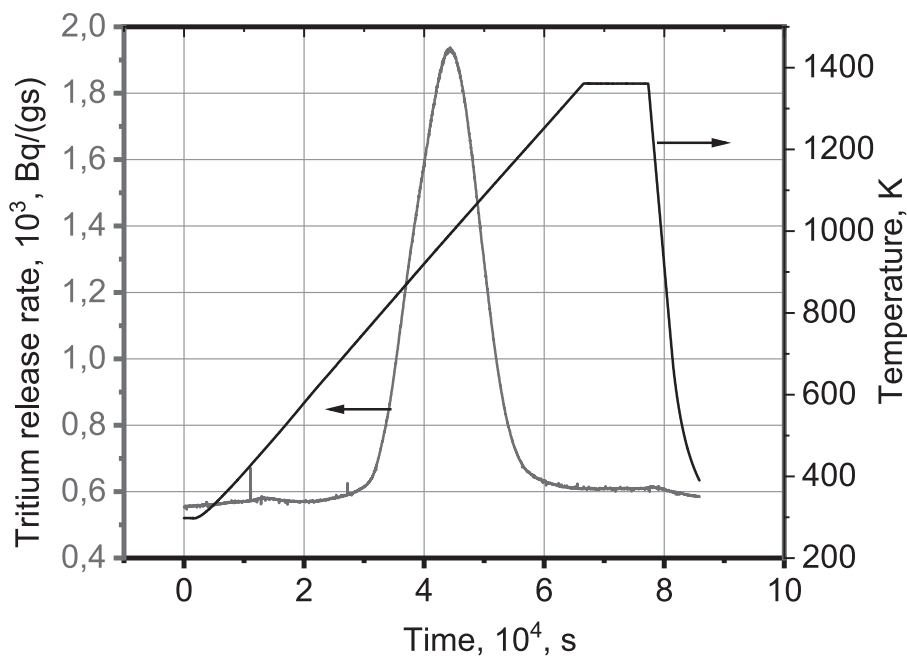
This relationship suggests that the extent of radiation-induced reduction in Be7Ti's thermal conductivity is directly linked to the proportion of the Be phase within the Be-Ti two-phase system. Fig. 6 provides an extrapolation to a single-phase Be-Ti material composed solely of the TiBe12 phase. This extrapolation predicts that the thermal conductivity of the irradiated TiBe12 phase falls within the range of 18–32 W/(m K) [23,24].

The Be7Ti two-phase structure, consisting of TiBe12 and Be phases, remains stable under high-dose neutron irradiation across all tested temperatures [24]. Notably, the Be-phase content does not change with varying irradiation temperatures. This stability is directly linked to the observed consistency in thermal conductivity across all irradiation conditions [24].

From this, it can be concluded that the extent of radiation-induced reduction in the thermal conductivity of Be7Ti is primarily determined



a



b

Fig. 2. Tritium release rate from Be (a) and Be7Ti (b) pellets irradiated at 783 K in the HIDOBE-01 tested at heating rate 1 K/min on time and temperature.

by the Be-phase content within the Be-Ti two-phase system. Fig. 6 illustrates an extrapolation to a hypothetical single-phase Be-Ti material composed entirely of the TiBe_{12} phase. Based on this extrapolation, the thermal conductivity of an irradiated TiBe_{12} -phase sample is estimated to fall within the range of 18–32 W/(m K) [23,24]. It can be seen that the thermal conductivity of both Be7Ti and the single-phase Be-Ti material after irradiation is higher than that of a beryllium pebble bed before irradiation (2–13 W/(m K) [25,26]).

3.4. Vickers microhardness

Fig. 7 presents the results of Vickers microhardness tests conducted on irradiated Be and Be7Ti pellets. These microhardness measurements in irradiated Be7Ti samples were carried out both on the large TiBe_{12} grains and on the thin layers of Be phase located between the titanium beryllide grains. The hardness measurements for irradiated Be pellets align well with previously reported data on Be pebbles irradiated in the

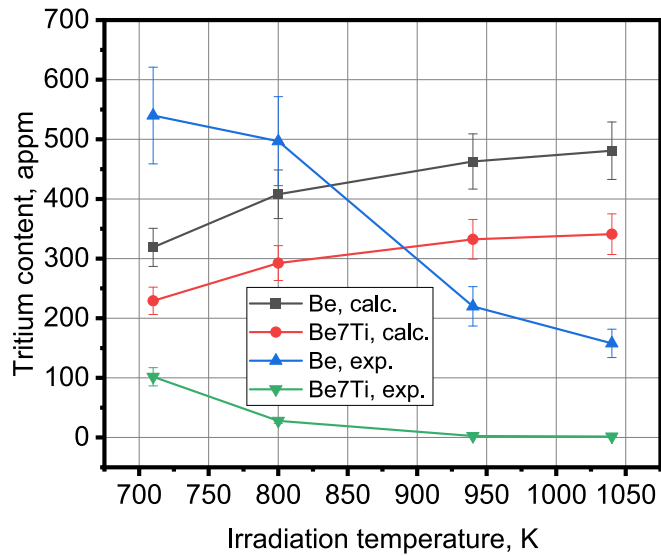


Fig. 3. Tritium content in Be and Be7Ti pellets versus irradiation temperature.

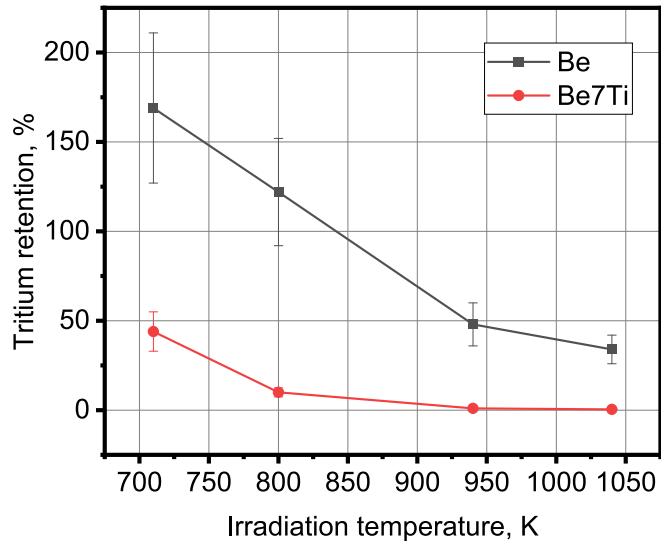


Fig. 4. Tritium retention in Be and Be7Ti pellets versus irradiation temperature.

HIDOBE-01 experiment [27]. However, the Be phase in Be7Ti samples exhibits significantly higher hardness compared to pure Be samples, surpassing it by a factor of two at the two highest irradiation temperatures.

The specific cause of this difference in hardness remains unclear. One possibility is that the internal stresses induced by beryllium swelling during irradiation may contribute to a comparatively greater radiation-induced hardness increase in the thin Be layers embedded between the surrounding TiBe₁₂ coarse grains, as opposed to freestanding Be samples. It is well established that beryllium undergoes rapid swelling at irradiation temperatures of approximately 800 K and above [28]. Nonetheless, it is evident that the TiBe₁₂ phase possesses a substantially higher microhardness than the Be phase. This characteristic is advantageous when considering the potential for manufacturing large-scale products from titanium beryllide.

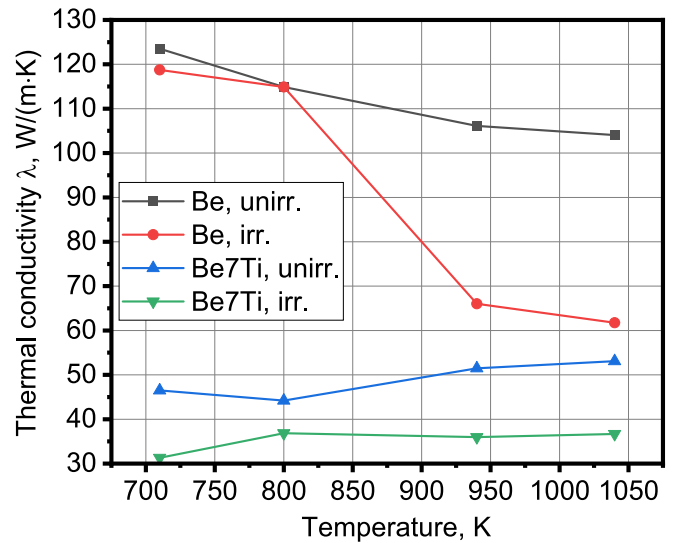


Fig. 5. Thermal conductivity λ of Be and Be7Ti pellets versus temperature ($T_{rest} = T_{irr}$).

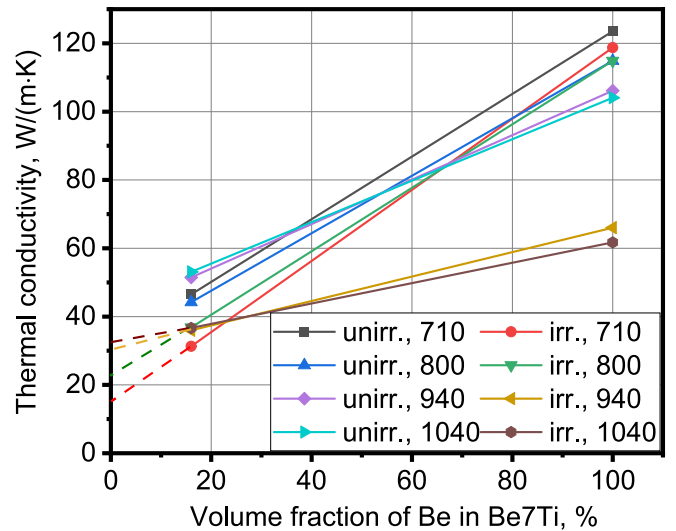


Fig. 6. Thermal conductivity of irradiated Be and Be7Ti samples versus volume fraction of Be-phase. The dashed lines show an extrapolation of thermal conductivity to 100 % of TiBe₁₂-phase content.

3.5. Microstructure evolution

3.5.1. Optical metallography (OM)

Fig. 8 illustrates the microstructure of Be7Ti samples after irradiation. Elongated TiBe₁₂ grains aligned along the electrode are visible (Fig. 8b). When viewed laterally, these elongated grains exhibit a regular shape (Fig. 8a). The two-phase structure predominantly consists of coarse TiBe₁₂ grains with thin interlayers of the Be phase (Fig. 8c). No significant changes in the phase structure were observed compared to the pre-irradiation state. The volume fraction of the Be phase in Be7Ti samples remains relatively stable (16–19 %) across all irradiation temperatures (see Fig. 9).

The formation of small bubbles, each significantly smaller than one micrometer, was identified exclusively within the Be phase at all irradiation temperatures. For example, Fig. 8c shows these small bubbles in the Be phase after irradiation at 1040 K. Cracks were also observed within the TiBe₁₂ grains. However, it remains uncertain whether these cracks developed during irradiation or resulted from cutting and

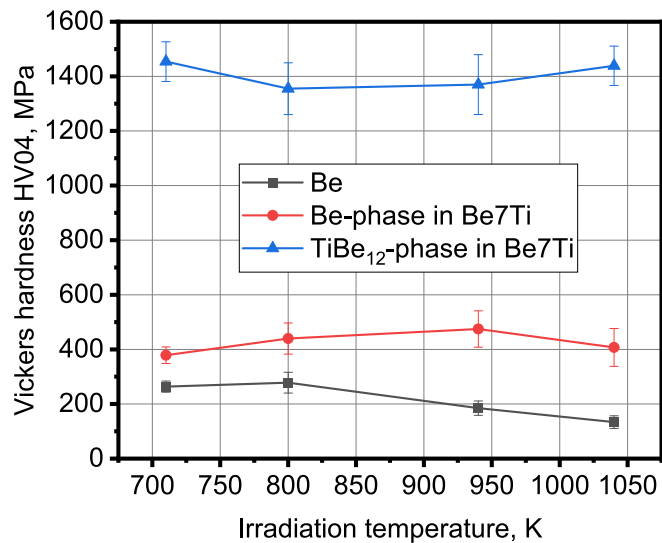


Fig. 7. Vickers microhardness of Be as well as the Be- and TiBe₁₂-phases in Be7Ti versus irradiation temperature.

preparing cross-sections of the irradiated Be7Ti samples for PIE, given the brittle nature of the TiBe₁₂ phase.

3.5.2. Transmission electron microscopy (TEM)

Figs. 10 and 11 show a typical microstructure of beryllium pebbles after neutron irradiation at 833 K [29–31]. Around the grain boundaries so called bubble denuded zones (DZ) with no or very few bubbles have formed (see Fig. 10a). These zones can have widths of >1 μm. While at higher irradiation temperatures of >723 K, there are usually no “free” precipitates within the matrix, impurities segregate at grain boundaries (see Fig. 10b) or at the basal planes of the hexagonal prismatic bubbles within the matrix. Fig. 11a shows the segregation of Al, Si and Mg at the basal planes of the hexagonal bubbles. The bubbles shape is illustrated in Fig. 11b. In contrast to Fe, the aforementioned elements show a strong binding energy of up to 1.0 eV [32] to vacancies within beryllium and therefore form halos around the bubbles (see Fig. 11c) [33].

In addition to the natural impurities the transmutant products helium and tritium are also trapped directly inside the bubbles. Electron energy loss spectroscopy (EELS) measurements revealed, that while helium is homogeneously distributed within the bubbles, tritium is strongly trapped at the basal (0001) planes (see Fig. 11d) [33,34]. In-situ heating experiments [33] suggest that tritium might be bound by a complex hydride at the inner bubble walls, which is stabilized by the large amounts of helium in the interior.

Figs. 12–14 show microstructure of Be7Ti pellet irradiated at 1040 K. Fig. 12a shows a TEM bright-field image of three adjacent TiBe₁₂ grains. From one of those grains the diffraction pattern shown in Fig. 12b was acquired along the TiBe₁₂ [101] zone-axis. The Be₁₂Ti grains (in dark contrast) are surrounded by pure Be (bright contrast). At the interface 100–200 nm sized bubbles are observed. In the TiBe₁₂ bubbles are hard to see at this magnification. Therefore, HRTEM images were acquired, as can be seen in Fig. 12c and 12d. Fig. 12c shows that in Be₁₂Ti bubbles are present like in pure Be. However, their size (about 15 nm in height and 5 nm in width) is smaller compared to pure Be irradiated at the same temperature. Fig. 12c was also used to determine the bubble number density as $(2.46 \pm 0.55) \cdot 10^{21} \text{ m}^{-3}$. Fig. 12d shows the bubbles in atomic resolution. The inset shows one bubble in an enlarged view. It is evident that the bubble surfaces running from top to bottom are atomically sharp. It can also be seen that those surfaces are decorated with something different than Ti due to the different contrast.

Fig. 13 shows a STEM-EDX elemental mapping in TiBe₁₂. It was found that the bubbles are decorated by Si atoms. The decoration layer

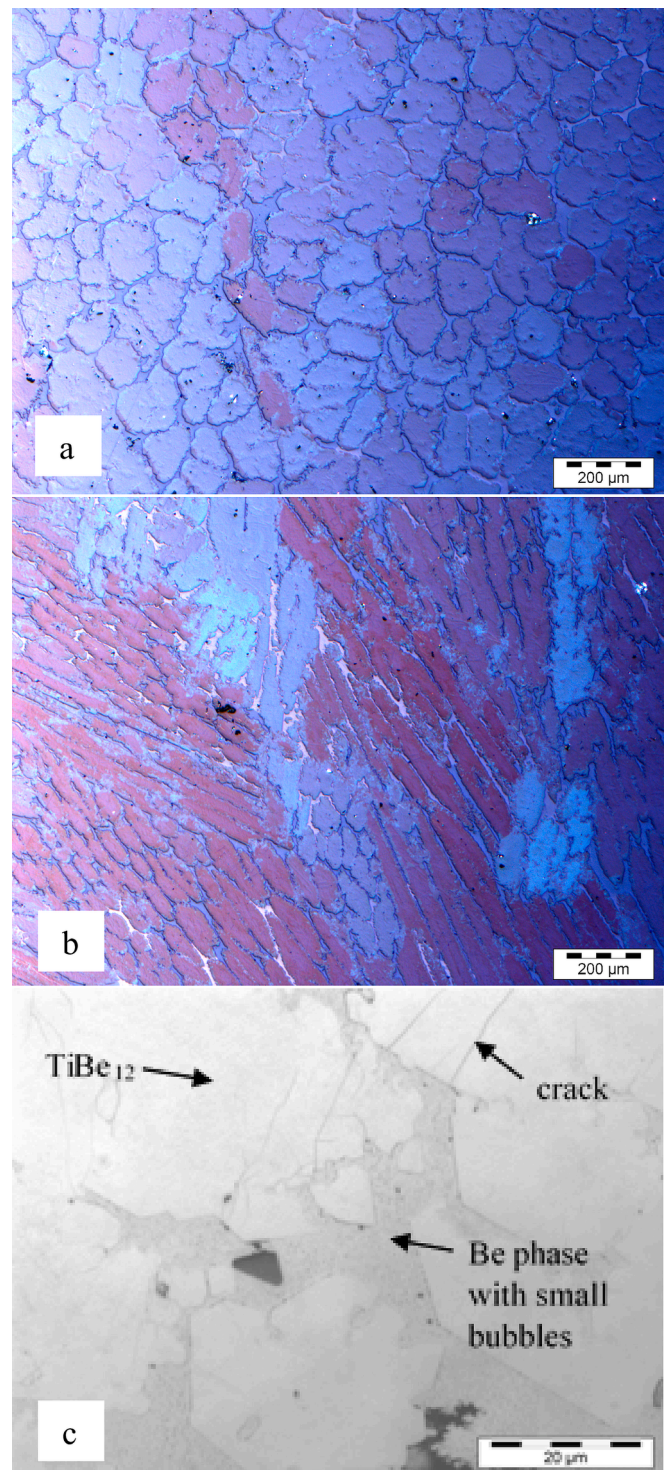


Fig. 8. Optical micrographs of two-phase composition in the irradiated Be7Ti pellets: a) $T_{\text{irr}} = 710 \text{ K}$, across electrode; b) $T_{\text{irr}} = 710 \text{ K}$, along electrode; c) $T_{\text{irr}} = 1040 \text{ K}$.

has a thickness of about 1.5 nm. This caused the different image contrast at the bubble surfaces in HRTEM images. Besides Si no other elements like for example Fe or U were found in TiBe₁₂ as it is the case in pure Be. This leaves the question of whether the bubbles in TiBe₁₂ are filled with tritium and helium like it is the case for pure Be.

Fig. 14 shows a STEM-EELS measurement on a single bubble in TiBe₁₂. The situation is comparable to pure Be, i.e. tritium is located at the bubble surfaces and helium fills the bubble volume. However, due to

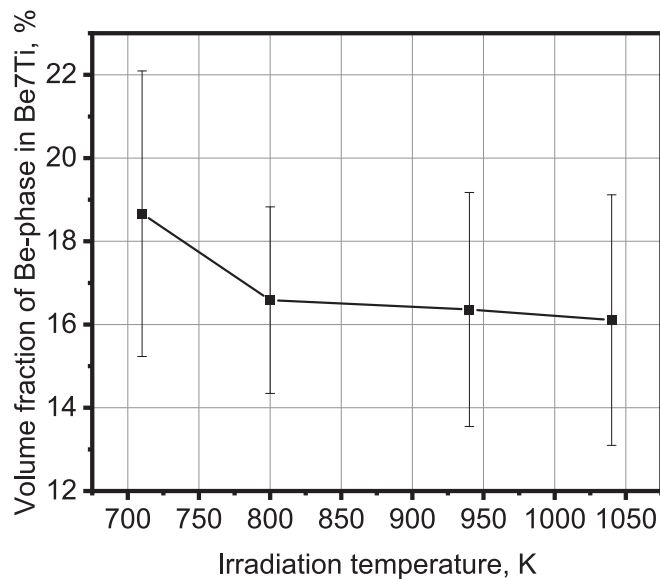


Fig. 9. Volume fraction of Be-phase in the Be7Ti samples versus irradiation temperature.

the small size of the bubble and the overall sample thickness the situation is less clear in TiBe_{12} than in pure Be. In the STEM-EELS spectra on the right-hand side of Fig. 14 the helium edge around 22 eV can be seen as small shoulder on the plasmon peak. For tritium there is only a peak broadening on the left-hand-side of the plasmon peak detected. Whether this is due to tritium or just an artifact remains unclear at present time.

4. Discussion

4.1. Comparison of beryllium and titanium beryllide based on PIEs results

The results after HIDOBE-01 and -02 experiments (see Figs. 3, 4) show that the tritium retention in Be is still high even at relatively large temperatures. For instance, Be still experiences a tritium retention of 40 % at 833 K, which is a temperature higher than the average of the Be pebble beds. Given that the temperature in the Be beds is limited to 923 K to avoid excessive swelling and loss of structural integrity in the pebbles, $\sim 2/3$ of the Be pebble bed is at a temperature of 773–873 K [35]. Therefore, the tritium inventory in Be at the blanket end of life may

likely exceed inventory safety limits. These limits are still not well defined for DEMO, but ITER currently considers a safety limit of 1 kg of in-vessel mobilizable tritium inventory [35]. Given the total volume of blanket that can be filled with Be pebbles and the given retention values, this safety limit would be easily breached. Therefore, the tritium retention in Be constitutes a critical issue of the HCPB DEMO design. Other problems associated with the use of Be pebbles is the water and air reactivity, problematic scalability of the production (difficult industrialization) and therefore, very high production costs.

Therefore, a key design change that was introduced during the major design change of the HCPB during the DEMO Pre-Conceptual Design Phase [36,37] has been the introduction of beryllides. These materials have demonstrated to have an excellent tritium release already at moderate temperatures, e.g. < 10 % at temperatures > 743 K and nearly 0 % at 823 K for BeTi type beryllides (see Fig. 4). Also, the swelling and reactivity of beryllides are significantly lower than for Be (e.g. swelling < 3 % for BeTi) (see Fig. 1). Therefore, the use of the BeTi material has been considered a must since then in order to mitigate the aforementioned critical issues linked with the use of pure Be as neutron multiplier material.

4.2. Evolution of HCPB from beryllium pebble bed to titanium beryllide massive block

The origin of the use of pebble beds in Be goes back to the DEMO studies in the 90 s under the EFDA framework. Originally, Be was proposed to be used in form of sintered blocks for the HCPB [1]. However, later research revealed critical issues using Be blocks due to the very large swelling rates of Be (>10 % already at temperatures > 773 K), as well as a severe neutron-induced embrittlement already at 10 % of the DEMO breeding blanket neutron fluence at low temperature (<373 K). In an attempt to mitigate these issues, accommodating the large swelling and reducing the effects of the possible disintegration of the Be blocks, Be in form of a pebble bed was introduced in the design of the HCPB and held up to the major design revision in 2018 [35]. Fig. 15 illustrates the proposed blanket module's configuration, resembling "sandwiches" comprised of alternating layers of beryllium pebbles and lithium ceramic pebbles. These layers are separated by EUROFER97 steel containing channels for helium cooling.

Concurrently, efforts were made to develop technologies for the industrial production of beryllium pebbles. The conventional method of casting beryllium pebbles, akin to casting lead shot in specialized towers, proved unviable due to several critical challenges. Beryllium's insufficient plasticity precluded the mechanical production of pebbles,

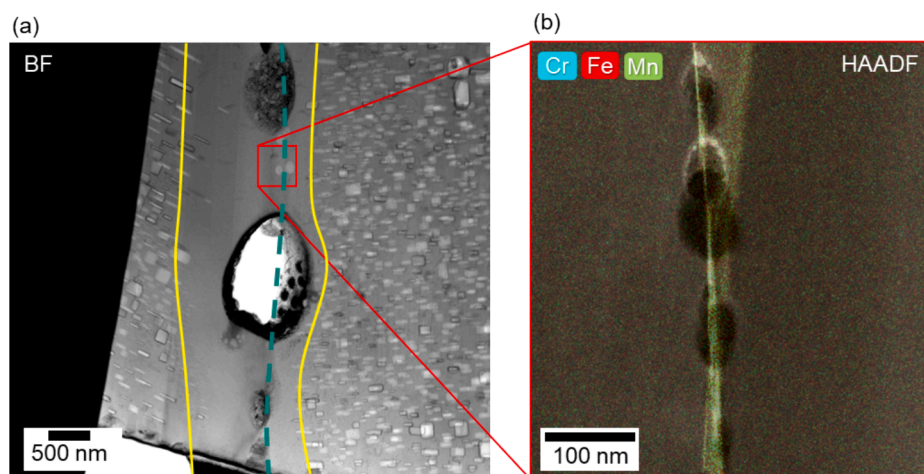


Fig. 10. A beryllium pebble microstructure after irradiation at 833 K: (a) Bright Field (BF) TEM image showing the formation of a denuded zone (DZ) around a grain boundary (green dashed line); (b) overlaid High Angular Annular Dark Field (HAADF) and EDX Scan showing the segregation of Cr, Fe and Mn around the grain boundaries.

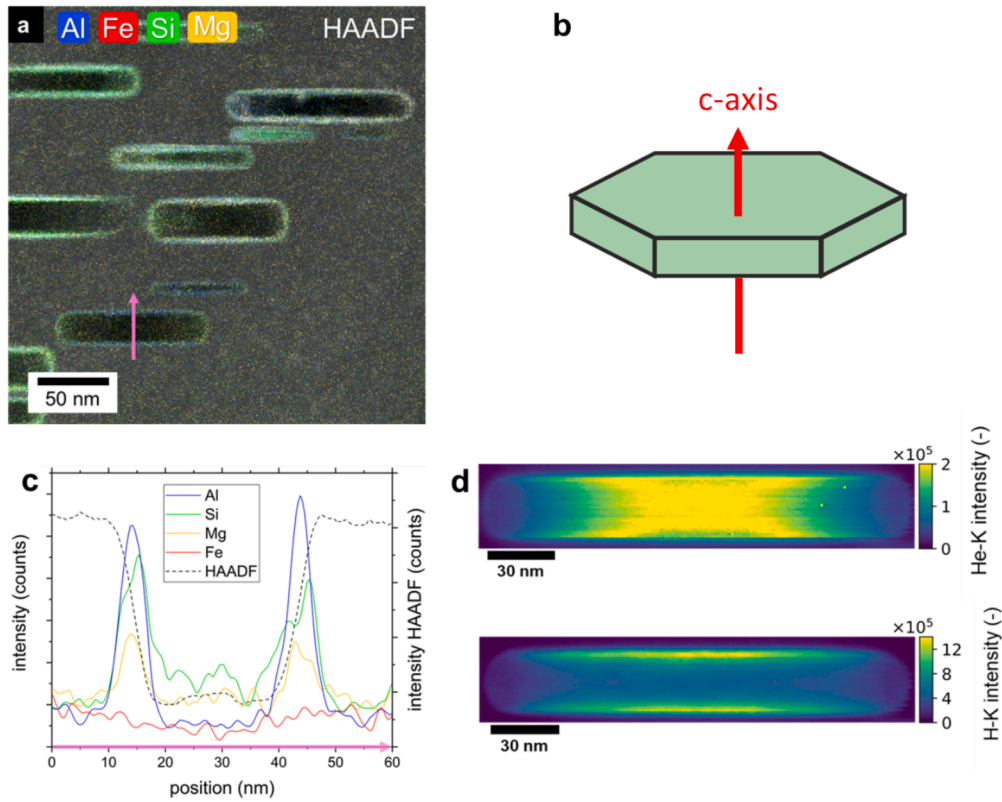


Fig. 11. Microstructure of beryllium pebble irradiated at 833 K: (a) segregation of natural impurities at the bubble walls; (b) schematic of the hexagonal prismatic disc shape of bubbles in neutron irradiated beryllium; (c) EDX intensity profile along the purple arrow shown in (a); (d) helium (top) and hydrogen (bottom) distribution within hexagonal prismatic bubbles. The helium intensity distribution follows the hexagonal prismatic shape of the bubble.

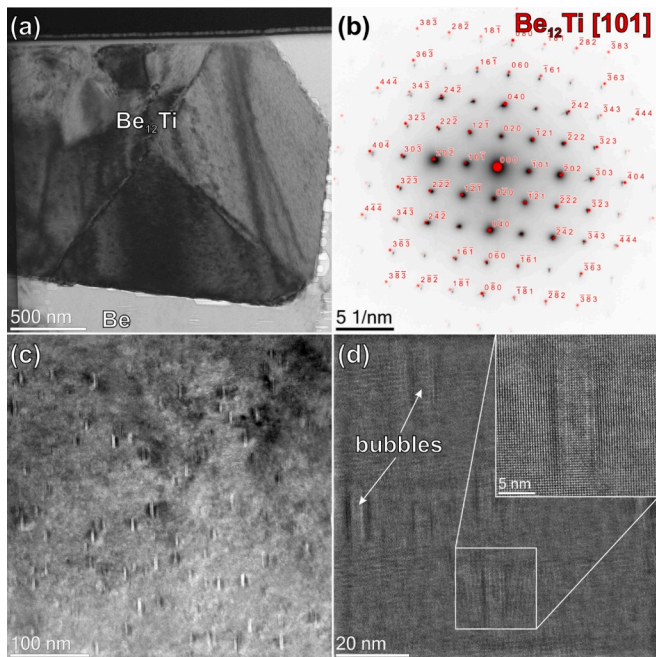


Fig. 12. A Be₇Ti pellet microstructure after irradiation at 1040 K: (a) bright-field TEM image of three TiBe₁₂ grains; (b) selected area diffraction pattern with an overlaid simulation along the TiBe₁₂ [101] zone-axis; (c) and (d) show high-resolution TEM images of TiBe₁₂. The inset in (d) shows a magnified view of a bubble in TiBe₁₂.

for instance, from beryllium wire or rods. Consequently, the rotating electrode method [38,39] emerged as the sole viable method for manufacturing beryllium pebbles. By carefully selecting rotation parameters and power input for melting, control over the resulting pebble size was attainable. Fig. 16 shows the appearance of beryllium pebbles produced through this method at NGK, Japan. In total, NGK manufactured approximately 30 kg of these pebbles, a portion of which was allocated for various studies, including neutron irradiation.

However, the issues of the large swelling and neutron-induced embrittlement and especially the tritium retention are largely mitigated if beryllides, e.g. TiBe₁₂, are used instead of Be. Following the analogy with beryllium pebbles, the initial plan was to replace beryllium in pebbles with titanium beryllide. This approach, for instance, is currently considered for the Japanese DEMO blanket. However, producing beryllide pebbles poses even greater challenges. Firstly, it necessitates higher temperatures, around 1873 K and above. During crystallization, titanium beryllide undergoes a peritectic transformation, leading to significant heterogeneity and porosity. Additionally, employing titanium beryllide as a pebble material inevitably results in a reduced tritium breeding ratio. Later internal feasibility assessments in KIT have concluded that the production of pebbles of TiBe₁₂ in the large amounts required for a HCPB breeding blanket load (several hundreds of tons) with the current technology (REM) seems to be unfeasible [35].

Upon obtaining results regarding the tritium content in beryllide samples after neutron irradiation and conducting a detailed microstructural study of irradiated beryllides [16,17,19–24,29–31], it became evident that there was no fundamental necessity to produce titanium beryllide in the form of pebbles. The need for a pebble bed is no longer justified if beryllides are used and slabs or blocks are again preferred, to be able to scale the production to very large volumes. This configuration of the neutron multiplier is the current one being considered for the reference HCPB design for DEMO [40,41]. Fig. 17 depicts the HCPB

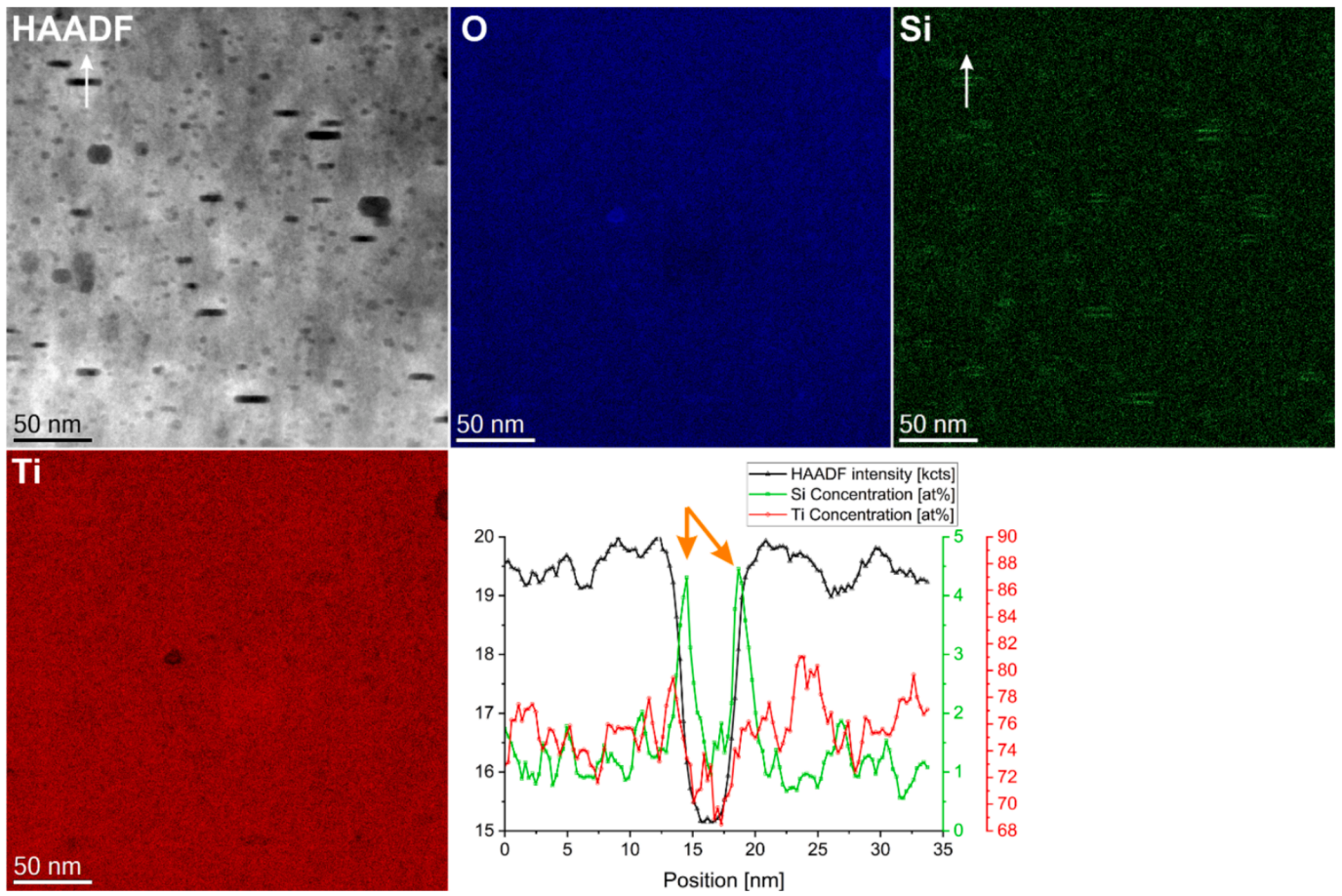


Fig. 13. STEM-EDX elemental mapping in $TiBe_{12}$ phase after irradiation at 1040 K.

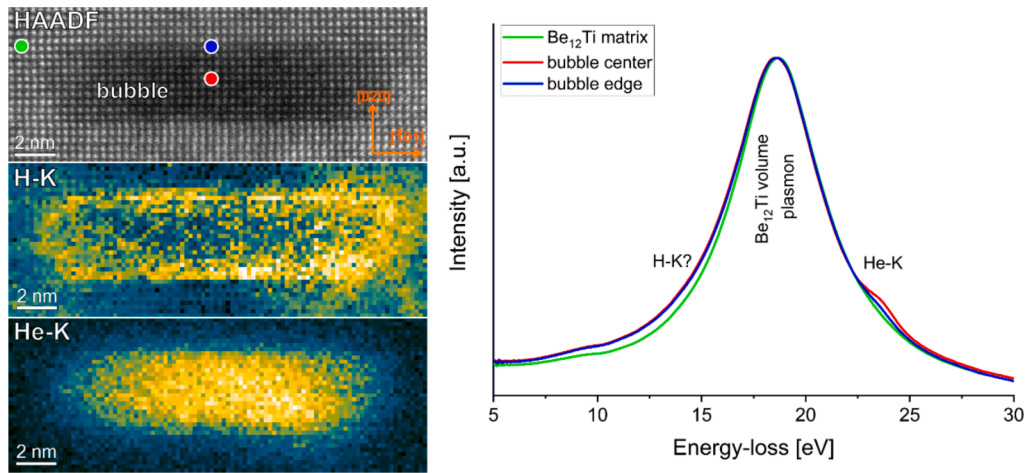


Fig. 14. STEM-EELS measurement on a single bubble in $TiBe_{12}$ phase after irradiation at 1040 K.

blanket design featuring a hexagonal pin configuration. Within these pins are lithium ceramic pebbles for tritium breeding, and the surrounding space must be filled with a neutron multiplier material, specifically massive blocks of titanium beryllide.

As of early 2019, production of massive beryllide blocks was non-existent worldwide. While research on beryllides was conducted in the USA during the 1960 s-1980 s, it primarily focused on relatively small blanks produced through methods like hot isostatic pressing (HIP) or vacuum hot pressing (VHP) [42].

KIT made significant advancements in the production of various

beryllides by employing hot extrusion of pure beryllium and titanium powders, followed by HIP, a process that allows for the simultaneous synthesis and consolidation of beryllides [43,44]. Optimal parameters for extrusion and HIP were established. However, the initial attempt at large-scale industrial HIP at the Ulba Metallurgical Plant (UMP) did not yield positive results, with the billet consistently experiencing cracking issues.

Instead, UMP proposed a two-stage method for producing blocks. In the initial stage, compressed tablets were created using a blend of beryllium and titanium powders. These tablets were then sintered in a

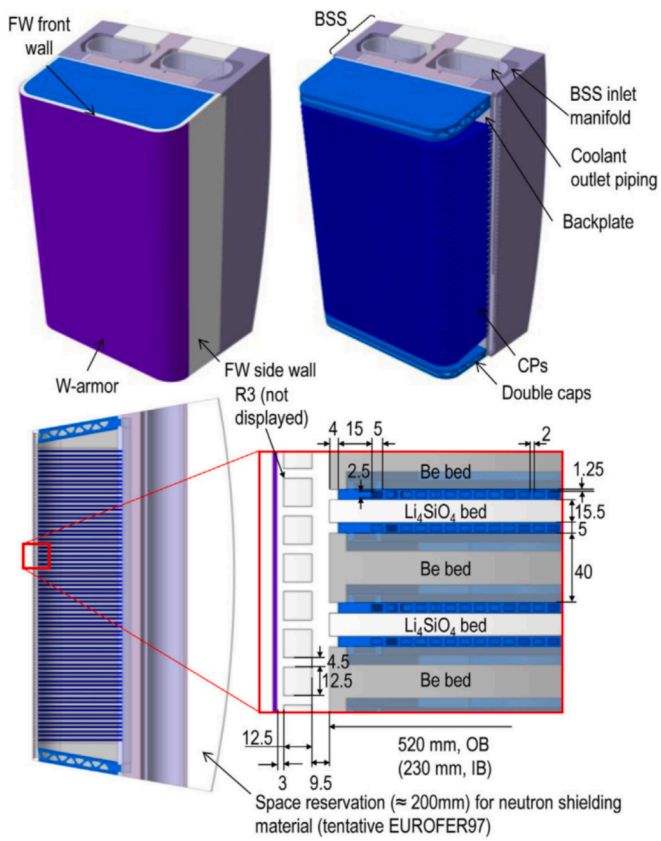


Fig. 15. HCPB DEMO breeding blanket employing beryllium pebbles as a neutron multiplication material.

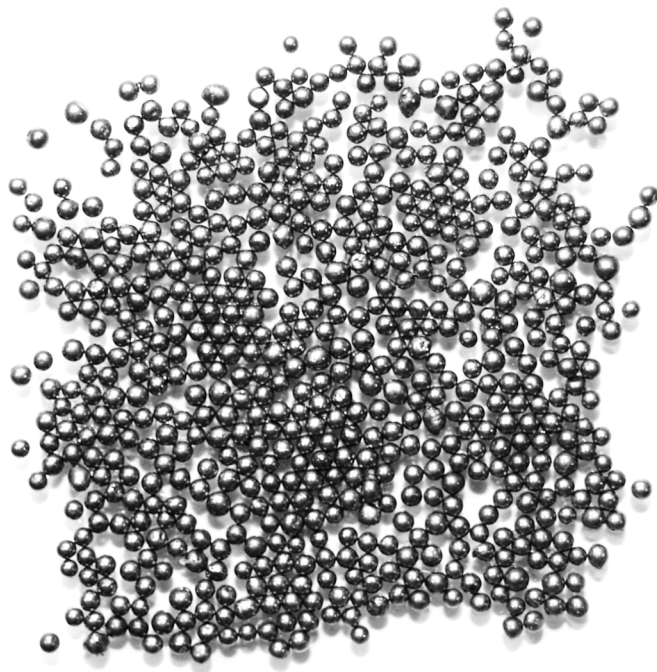


Fig. 16. Beryllium pebbles, approximately 1 mm in size, produced using the rotating electrode method at NGK, Japan.

vacuum furnace to synthesize titanium beryllide. Subsequently, the tablets were ground into powder, and vacuum hot pressing was employed to shape the titanium beryllide powder. Through this process,

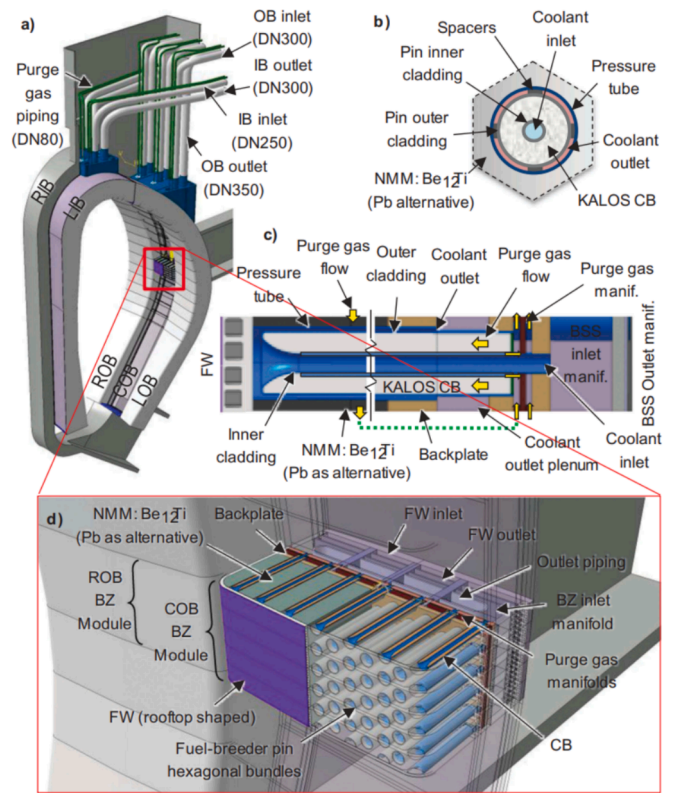


Fig. 17. Enhanced HCPB DEMO breeder blanket concept with fuel-breeder pins: (a) one sector showing the right-inboard, left-inboard, center outboard, and left outboard segments; (b) transversal cross-section view of a fuel-breeder pin; (c) longitudinal cross-section view of a fuel-breeder pin; (d) isometric cut-out view of a center-outboard fuel-breeder pin assembly (NMM is neutron multiplier material).

the first substantial blanks, measuring 150 mm in diameter and 170 mm in height, were manufactured. These blanks served for producing full-sized blocks measuring 144 mm in diameter and 150 mm in height (see Fig. 18) [45].

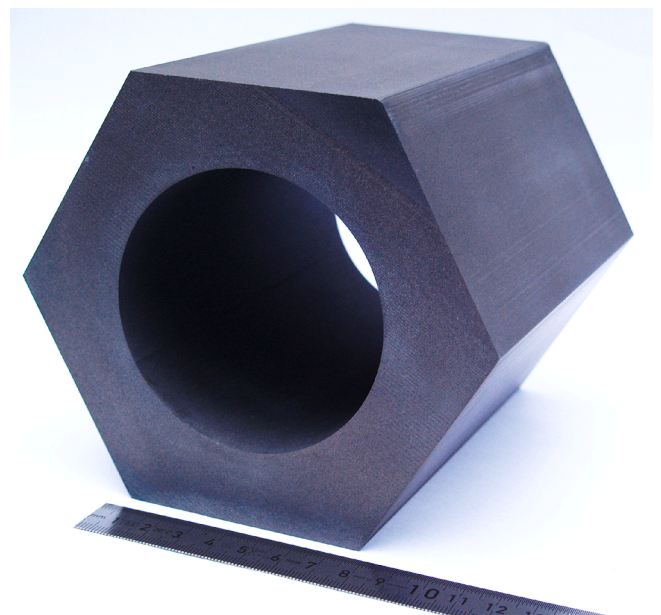


Fig. 18. Titanium beryllide block, measuring $\varnothing 144\text{mm} \times 150\text{mm}$, fabricated by vacuum hot pressing at UMP, Kazakhstan.

An additional challenge was the creation of an 80 mm central hole in the extremely hard and brittle beryllide material. Conventional mechanical drilling proved to be time-consuming and labor-intensive, while waterjet cutting was inefficient and inaccurate for blocks of such considerable height. Consequently, the electrical discharge machining method was utilized for processing.

As of mid-2023, significant advancements have been made in block manufacturing technology at UMP. Specifically, it became possible to consolidate the operations for beryllide synthesis and vacuum hot pressing, resulting in cost reduction. In total, approximately 20 blocks of titanium beryllide and around 10 blocks of chromium beryllide were produced [46].

Chromium beryllide was selected as an alternative material in case any significant, insurmountable drawbacks with titanium beryllide arose, a scenario which, at the time of writing, has not occurred and is considered unlikely. Initial attempts to utilize beryllide scraps as waste material also proved successful. This approach not only further diminishes the cost of blocks due to increased utilization of residual material but also opens up prospects for beryllide recycling after its initial use.

5. Conclusions and outlook

A large-scale irradiation experiment, including the HIDOBE-01 and -02 campaigns conducted by the fusion research community between 2005 and 2011, along with subsequent post-irradiation examinations (PIEs) of Be-based materials (pure beryllium in the form of pebbles/pellets and titanium beryllide in the form of pellets), led to several key conclusions and significant modifications to the original HCPB DEMO breeding blanket concept.

Beryllium pebbles exhibit high swelling and tritium retention, along with poor mechanical properties after high-dose neutron irradiation at relevant operational temperatures. Additionally, the industrial-scale production of beryllium pebbles is both costly and technologically challenging.

In contrast, titanium beryllide demonstrates significantly lower swelling and tritium retention, as well as superior mechanical strength at considerably higher operating temperatures.

These findings provided the theoretical and computational foundation to modernize the HCPB DEMO breeding blanket concept by replacing beryllium pebbles as the neutron multiplier with massive blocks of titanium beryllide.

A production technology for large titanium beryllide blocks has been developed, resulting in the fabrication of several blocks with complex geometric shapes. The feasibility of industrial-scale production of these blocks has also been demonstrated.

Future efforts should focus on optimizing the production technology to reduce costs and conducting studies on full-scale titanium beryllide blocks under operational conditions, including thermal cycling and other relevant factors, to further validate their suitability for DEMO applications.

CRedit authorship contribution statement

Vladimir Chakin: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Conceptualization. **Rolf Rolli:** Writing – review & editing, Investigation. **Hans-Christian Schneider:** Methodology, Investigation, Formal analysis. **Ramil Gaisin:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Pavel Vladimirov:** Writing – review & editing, Methodology, Formal analysis, Conceptualization. **Michael Klimenkov:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Conceptualization. **Michael Duerrschnebel:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Conceptualization. **Nikolai Zimmer:** Writing – review & editing, Methodology, Investigation. **Michael Rieth:** Writing –

review & editing, Project administration, Methodology, Funding acquisition, Conceptualization. **Bronislava Gorr:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization. **Francisco A. Hernández:** Writing – review & editing, Validation, Funding acquisition, Formal analysis, Conceptualization. **Dirk Radloff:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization. **Alexander Fedorov:** Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Milan Zmitko:** Writing – review & editing, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Masaru Nakamichi:** Writing – review & editing, Validation, Investigation, Formal analysis, Conceptualization. **Sergey Udartsev:** Writing – review & editing, Methodology, Investigation, Conceptualization.

Declaration of competing interest

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.

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Data availability

No data was used for the research described in the article.

References

- [1] M. Dalle Donne, E. Bojarsky, U. Fischer, M. Kuechle, P. Norajitra, J. Reimann, H. Reiser, H.D. Baschek, E. Bogusch, The Karlsruhe solid breeder blanket and the test module to be irradiated in ITER/NET, *Fusion Eng. Des.* 87 (1991) 87–94.
- [2] E. Proust, L. Anzidei, G. Casini, M. Dalle Donne, L. Giancarli, S. Malang, Breeding blanket for DEMO, *Fusion Eng. Des.* 22 (1993) 19–33.
- [3] M. Dalle Donne, D.R. Harries, G. Kalinin, R. Mattas, S. Mori, Material problems and requirements related to the development of fusion blankets: the designer point of view, *J. Nucl. Mater.* 212–215 (1994) 69–79.
- [4] M. Dalle Donne, G.R. Longhurst, H. Kawamura, F. Scaffidi-Argentina, Beryllium R&D for blanket application, *J. Nucl. Mater.* 258–263 (1998) 601–606.
- [5] F. Scaffidi-Argentina, M. Dalle Donne, H. Werle, Critical assessment of beryllium pebbles response under neutron irradiation: Mechanical performance and tritium release, *J. Nucl. Mater.* 258–263 (1998) 595–600.
- [6] F. Scaffidi-Argentina, G.R. Longhurst, V. Shestakov, H. Kawamura, Beryllium R&D for fusion applications, *Fusion Eng. Des.* 51–52 (2000) 23–41.
- [7] F. Scaffidi-Argentina, Tritium and helium release from neutron irradiated beryllium pebbles from the EXOTIC-8 irradiation Fusion, *Eng. Des.* 58–59 (2001) 641–645.
- [8] H. Kawamura, H. Takahashi, N. Yoshida, V. Shestakov, Y. Ito, M. Uchida, H. Yamada, M. Nakamichi, E. Ishitsuka, Application of beryllium intermetallic compounds to neutron multiplier of fusion blanket, *Fusion Eng. Des.* 61–62 (2002) 391–397.
- [9] H. Kawamura, H. Takahashi, N. Yoshida, Y. Mishima, K. Ishida, T. Iwadachi, A. Cardella, J.G. van der Laan, M. Uchida, K. Munakata, Y. Sato, V. Shestakov, S. Tanaka, Present status of beryllide R&D as neutron multiplier, *J. Nucl. Mater.* 329–333 (2004) 112–118.
- [10] H. Iwakiri, K. Yasunaga, N. Yoshida, M. Uchida, H. Kawamura, Thermal desorption of deuterium from ion irradiated Be₁₂Ti, *J. Nucl. Mater.* 329–333 (2004) 880–884.
- [11] M. Uchida, E. Ishitsuka, H. Kawamura, Thermal conductivity of neutron irradiated Be₁₂Ti, *Fusion Eng. Des.* 69 (2003) 499–503.
- [12] M. Nakamichi, H. Kawamura, M. Uchida, Compatibility test between Be₁₂Ti and Li₂TiO₃, *Fusion Eng. Des.* 69 (2003) 257–261.
- [13] K. Tsuchiya, H. Kawamura, T. Ishida, Compatibility between Be-Ti alloys and F82H steel, *J. Nucl. Mater.* 367–370 (2007) 1018–1022.
- [14] J.B.J. Hegeman, J.G. van der Laan, H. Kawamura, A. Moeslang, I. Kupriyanov, M. Uchida, K. Hayashi, The HFR Petten high dose irradiation programme of beryllium for blanket application, *Fusion Eng. Des.* 75–79 (2005) 769–773.
- [15] V. Chakin, R. Rolli, A. Moeslang, P. Kurinskiy, Tritium and helium release from highly neutron irradiated titanium beryllide, *Fusion Eng. Des.* 98–99 (2015) 1728–1732.

- [16] V. Chakin, R. Rolli, R. Gaisin, U. Hoepfener-Kramar, M. Nakamichi, M. Zmitko, Tritium release and retention in beryllium and titanium beryllide after neutron irradiation up to damage doses of 23-38 dpa, *Fusion Eng. Des.* 161 (2020) 111938.
- [17] V. Chakin, R. Rolli, M. Klimenkov, M. Zmitko M., Tritium release and retention in beryllium pebbles irradiated up to 640 appm tritium and 6000 appm helium, *J. Nucl. Mater.* 542 (2020) 152521.
- [18] D.N. Syslov, V.P. Chakin, R.N. Latypov, Influence of high dose neutron irradiation on thermal conductivity of beryllium, *J. Nucl. Mater.* 307–311 (2002) 664–667.
- [19] V. Chakin, A. Fedorov, R. Gaisin, M. Zmitko, Swelling of highly neutron irradiated beryllium and titanium beryllide, *J. Nucl. Eng.* 3 (4) (2022) 398–408.
- [20] A.V. Fedorov, S. van Til, M.P. Stijkel, M. Nakamichi, M. Zmitko, Post irradiation characterization of beryllium and beryllides after high temperature irradiation up to 3000 appm helium production in HIDOBE-01, *Fusion Eng. Des.* 102 (2016) 74–80.
- [21] V. Chakin, R. Rolli, A. Moeslang, M. Klimenkov, M. Kolb, P. Vladimirov, P. Kurinskiy, H.-C. Schneider, S. van Til, A.J. Magielsen, M. Zmitko, Tritium release and retention properties of highly neutron-irradiated beryllium pebbles from HIDOBE-01 experiment, *J. Nucl. Mater.* 442 (2013) S483–S489.
- [22] A.V. Fedorov, S. van Til, L.J. Magielsen, M.P. Stijkel, Analysis of tritium retention in beryllium pebbles in EXOTIC, PBA and HIDOBE-01 experiments, *J. Nucl. Mater.* 442 (2013) 472–477.
- [23] V. Chakin, J. Reimann, A. Moeslang, R. Latypov, A. Obukhov, Thermal conductivity of highly neutron-irradiated beryllium in nuclear fusion reactors, *Progress in Nucl. Ener.* 57 (2012) 2–7.
- [24] V. Chakin, A. Fedorov, R. Rolli, R. Gaisin, M. Klimenkov, J. Reimann, M. Nakamichi, Thermal conductivity of high-dose neutron irradiated beryllium and titanium beryllide, *J. Nucl. Mater.* 559 (2022) 153430.
- [25] G. Piazza, J. Reimann, G. Hofmann, S. Malang, A.A. Goraieb, H. Harsch, Heat transfer in compressed beryllium pebble beds, *Fusion Eng. Des.* 69 (2003) 227–231.
- [26] J. Reimann, G. Piazza, H. Harsch, Thermal conductivity of compressed beryllium pebble beds, *Fusion Eng. Des.* 81 (2006) 449–454.
- [27] V. Chakin, R. Rolli, A. Moeslang, P. Vladimirov, P. Kurinskiy, S. van Til, A. J. Magielsen, M. Zmitko, Characterization of constrained beryllium pebble beds after neutron irradiation at HFR at high temperatures up to helium production of 3000 appm, *Fusion Eng. Des.* 88 (2013) 309–313.
- [28] S. van Til, J.B.J. Hegeman, H.L. Cobussen, M.P. Stijkel, Evolution of beryllium pebbles (HIDOBE) in long term, high flux irradiation in the high flux reactor, *Fusion Eng. Des.* 86 (2011) 2258–2261.
- [29] N. Zimber, P. Vladimirov, M. Klimenkov, V. Kuksenko, Investigation of a high-dose irradiated beryllium microstructure, *J. Nuc. Mater.* 540 (2020) 152374.
- [30] N. Zimber, *Nanoskalige Analytik der Mikrostruktur von hochdosig bestrahltem Beryllium*, KIT Scientific Publishing, Karlsruhe (2022).
- [31] N. Zimber, P. Vladimirov, M. Duerrschabel, M. Klimenkov, J. Lammer, S. Kuksenko, G. Kothleitner, Investigation of a high-dose irradiated beryllium microstructure including a STEM-EELS analysis of helium/tritium-bubbles, *Konferenzabstract für European Microscopy Congress, Kopenhagen (2020)*, <https://doi.org/10.22443/rms.emc2020.282>.
- [32] M. Klimenkov, P. Vladimirov, U. Jaentsch, V. Kuksenko, R. Rolli, A. Moeslang, N. Zimber, New insights into microstructure of irradiated beryllium based on experiments and computer simulations, *Sci. Rep.* 10 (2020) 8042, <https://doi.org/10.1038/s41598-020-64654-5>.
- [33] N. Zimber, J. Lammer, P. Vladimirov, G. Kothleitner, V.J. Keast, M. Duerrschabel, M. Klimenkov, Hydrogen and helium trapping in hcp beryllium, *Commun. Chem.* 6 (2023) 76, <https://doi.org/10.1038/s42004-023-00877-7>.
- [34] M. Klimenkov, P. Vladimirov, J. Hoffmann, N. Zimber, A. Moeslang and V. Kuksenko, First simultaneous detection of helium and tritium inside bubbles in beryllium Micron (Oxford, England 1993) 127 (2019) 102754 doi: 10.1016/j.micron.
- [35] F. Hernández, P. Pereslavtsev, Q. Kang, P. Norajitra, D. Kiss, G. Nádasi, O. Bitz, A new HCPB breeding blanket for the EU DEMO: evolution, rationale and preliminary performances, *Fusion Eng. Des.* 124 (2017) 882–886, <https://doi.org/10.1016/j.fusengdes.2017.02.008>.
- [36] F.A. Hernández, et al., An enhanced near-term HCPB configuration as driver blanket for the EU DEMO, *Fusion Eng. Des.* 146 (A) (2019) 1186–1191.
- [37] R. Knitter et al., *Functional Materials in Blankets – Status, Implications and Needs*, European Fusion Program Workshop (2018), Bad Dürkheim, Germany.
- [38] E. Ishitsuka, H. Kawamura, N. Sakamoto and K. Nishida, Process for preparing metallic beryllium pebbles US Patent 5958105 (1999).
- [39] E. Ishitsuka, H. Kawamura, T. Terai, S. Tanaka, Microstructure and compression properties of neutron irradiated beryllium, *J. Nucl. Mater.* 258–263 (1998) 566–570.
- [40] F.A. Hernández, et al., Consolidated design of the HCPB breeding blanket for the pre-conceptual design phase of the EU DEMO and harmonization with the ITER HCPB TBM program, *Fusion Eng. Des.* 156 (2020) 111614.
- [41] F.A. Hernández, P. Pereslavtsev, G. Zhou, B. Kiss, Q. Kang, H. Neuberger, V. Chakin, R. Gaisin, P. Vladimirov, L.V. Boccaccini, G.A. Spagnuolo, S. D'Amico, I. Moscato, Advancements in the helium-cooled pebble bed breeding blanket for the EU DEMO: holistic design approach and lessons learned fusion, *Sc Techn.* 75 (5) (2019) 352–364, <https://doi.org/10.1080/15361055.2019.1607695>.
- [42] K.A. Walsh, *Beryllium Chemistry and Processing*, ASM International 2009.
- [43] R. Gaisin, V. Chakin, M. Duerrschabel, R. Rolli, T. Weingaertner, A. Goraieb, P. Vladimirov, Effect of HIP at 800 and 900 °C on microstructure and properties of extruded Be-Ti composites, *Nucl. Mater. Energy* 24 (2020) 100771.
- [44] R. Gaisin R., V. Kuksenko, M. Duerrschabel, V. Chakin, A. Goraieb and P. Vladimirov, Effect of HIP at 1000–1200 °C on microstructure and properties of extruded Be-Ti composites *Nucl. Mater. Energy* 30 (2022) 101128.
- [45] R. Gaisin, V. Chakin, P. Vladimirov, F.A. Hernández, S. Udartsev, A. Vechkutov, M. Kolmakov, Industrial-scale manufacturing experience of titanium beryllide block for DEMO blanket application, *Fusion Eng. Des.* 161 (2020) 111862, <https://doi.org/10.1016/j.fusengdes.2020.111862>.
- [46] R. Gaisin, Ye. Frants, M. Kolmakov, B. Zorin, M. Kylyshkanov, M. Podoinikov, S. Udartsev, A. Vechkutov, V. Chakin and P. Vladimirov, Beryllium intermetallics: Industrial experience on development and manufacture, *Nucl. Mater. Energy* 35 (2023) 101444 ISSN2352-1791 doi: 10.1016/j.nme.2023.101444.