

Behaviour of advanced tritium breeder pebbles under simultaneous action of accelerated electrons and high temperature

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h i g h l i g h t s

- Irradiation temperature affects accumulation of radiation-induced defects (RD) and radiolysis products (RP).
- With an increasing content of Li₂ TiO₃ in the advanced pebbles, the concentration of accumulated RD and RP decreases.
- The accumulated RD and RP annihilates around 423–773 K.
- Mechanical properties of the advanced pebbles practically do not change after irradiation.

Advanced lithium orthosilicate (Li₄ SiO₄) pebbles with additions of lithium metatitanate (Li₂ TiO₃) as a secondary phase are suggested as a potential source for tritium breeding in future nuclear fusion reactors. The advanced Li₄ SiO₄ pebbles with different contents of Li₂ TiO₃ were examined before and after simultaneous action of 5 MeV accelerated electron beam (dose rate: up to 10 MGy h⁻¹) and high temperature (up to 1120 K) in a dry argon atmosphere. The accumulated radiation-induced defects (RD) and radiolysis products (RP) were studied by electron spin resonance (ESR) spectrometry and thermally stimulated luminescence (TSL) technique. The phase transitions were studied with powder X-ray diffraction (p-XRD). The microstructure and mechanical strength of the pebbles, before and after irradiation, were investigated by scanning electron microscopy (SEM) and comprehensive crush load tests. The obtained results revealed that the irradiation temperature has a significant impact on the accumulation of RD and RP in the advanced Li₄ SiO₄ pebbles, and with an increasing content of Li₂ TiO₃, the concentration of accumulated paramagnetic RD and RP decreases. Major changes in the mechanical strength, microstructure and phase composition of the advanced pebbles were not detected after irradiation.

1. Introduction

Lithium orthosilicate (Li₄ SiO₄) and lithium metatitanate (Li₂ TiO₃) in the form of ceramic pebbles have been developed as two of the most promising tritium breeder candidates for future nuclear fusion reactors [1]. Under the operation conditions of the fusion reactors, the tritium breeder pebbles will be exposed to an intense neutron fluence (up to 10¹⁸ n m⁻² s⁻¹), a high temperature (up to 1193 K) and a magnetic field (up to 7–10 T) [2]. The latest results of the post-irradiation examination [3] confirmed that both tritium breeder pebbles will perform sufficiently well under the expected operation conditions. However, it has also been reported that the mechanical properties of pure Li₄ SiO₄ pebbles need to be improved, while Li₂ TiO₃ pebbles require a higher enrichment with lithium-6, to increase tritium production.

Table 1

Specification of the investigated advanced Li₄ SiO₄ pebbles with different contents of Li₂ TiO₃ and the reference pebbles.

Sample	Pebbles	Phase compositions			Pebble size (μm)	Description
		Li ₄ SiO ₄ , mol%	Li ₂ TiO ₃ , mol%	Li ₂ SiO ₃ , mol%		
#0	Reference	90	0	10	500 650–900	Un-treated Thermally pre-treated
#1	Advanced	90	10	0	1000 650–900	Un-treated Thermally pre-treated
#2	Advanced	80	20	0	500 650–900	Un-treated Thermally pre-treated
#3	Advanced	75	25	0	500	Un-treated
#4	Advanced	70	30	0	500 650–900	Un-treated Thermally pre-treated
#5	Advanced	60	40	0	1000	Thermally pre-treated

The advanced Li₄ SiO₄ pebbles with additions of Li₂ TiO₃ as a secondary phase have been proposed as an alternative candidate for the tritium breeding [4]. The optimum content of Li₂ TiO₃ has yet to be evaluated; nonetheless the advanced pebbles have enhanced mechanical properties, without losing the benefit of a high lithium density and melting temperature [5]. The preliminary studies indicate that the change in the chemical composition of the pebbles does not significantly affect the radiation stability [6], release characteristics [7] and activation behaviour [8]. The re-melting and lithium re-enrichment studies [9] also revealed that the recycling of the advanced breeder pebbles, without a deterioration of the material properties, is possible using an enhanced melt-based process.

However, to develop a new two-phase composition for the tritium breeder pebbles, it is a critical issue to study the behaviour of the advanced Li₄ SiO₄ pebbles under the simultaneous action of radiation, temperature and magnetic field. From previous long-term irradiation studies [10,11], it is known that under such conditions various physicochemical processes (lithium burn-up, atomic displacements, radiation-induced chemical processes and phase transitions) can take place and thus affect the phase composition and microstructure, as well as the thermal and mechanical properties of the breeder pebbles. The accumulated radiation-induced defects (RD) and radiolysis products (RP) may interact with generated tritium and strongly influence the tritium transport and release processes [12–14]. Previously, the correlation between the tritium release processes and the thermal annealing of RD and RP have been detected [15] and it has been assumed that the recombination of RD and RP could trigger the tritium detrapping.

We herein report on the behaviour of the advanced Li₄ SiO₄ pebbles with various contents of Li₂ TiO₃ considering simultaneous action of 5 MeV accelerated electron beam (dose rate: up to 10 MGy h⁻¹) and high temperature (up to 1120 K) in dry argon atmosphere, to predict the tritium diffusion and release mechanisms. Such study was performed by means of electron spin resonance (ESR), powder X-ray diffraction (p-XRD), thermally stimulated luminescence (TSL) and scanning electron microscopy (SEM) techniques and, as a preliminary approach, only the flux of accelerated electrons was used instead of neutron irradiation, to introduce RD and RP while avoiding nuclear reactions and thereby the formation of radioactive isotopes. The irradiation temperature was chosen in order to reach conditions comparable to the operation conditions of the fusion nuclear reactor.

2. Experimental

The advanced Li₄ SiO₄ pebbles with five different contents of Li₂ TiO₃ were selected for this research together with the reference pebbles (Table 1). The reference pebbles (0 mol% Li₂ TiO₃) consist of two main phases – Li₄ SiO₄ as the primary and lithium metasilicate (Li₂ SiO₃) as a secondary phase, and they are the present reference material for tritium breeding in the EU developed con-

cept [1]. The advanced pebbles were produced by an enhanced melt-based process at the Karlsruhe Institute of Technology (Karlsruhe, Germany) [4], while the reference pebbles were fabricated by a melt-spraying method at Schott AG (Mainz, Germany) [16]. To achieve an operation relevant microstructure, the fabricated advanced and reference pebbles were thermally pre-treated at 1223 K for 504 h in air.

Both, the un-treated and thermally pre-treated Li₄ SiO₄ pebbles with different contents of Li₂ TiO₃ were encapsulated in quartz tubes with a dry argon and were irradiated with the linear electron accelerator ELU-4 (Salaspils, Latvia), up to 4 h per day (Table 2). During one irradiation campaign (three irradiation cycles) with 5 MeV accelerated electrons, up to 100 MGy absorbed dose (dose rate: <10 MGy h⁻¹), up to four quartz tubes were irradiated simultaneously. The electron beam diameter is around 40 mm and to avoid differences in the absorbed dose depending on tube location in the irradiation area, the location of each tube was changed after each irradiation cycle. Due to the collision of accelerated electrons with quartz tubes and pebbles, most of the kinetic energy of the accelerated electrons is transferred into heat within the specimen, causing a local temperature rise (up to 1120 K). Therefore, the irradiation temperature was continuously measured by a chromel-alumel thermocouple, that was located in central part of irradiated area, with an Agilent 34970 A multichannel digital voltmeter and an Agilent 34902 A multiplexer and recorded with a PC using the Agilent BenchLink Data Logger 3 software. The measured temperature differences between separate irradiation cycles could be associated with beam center displacement, linear electron accelerator current or voltage changes etc.

The accumulated paramagnetic RD and RP were investigated by ESR spectrometry. The ESR spectra were recorded using Bruker BioSpin X-band ESR spectrometer (microwave frequency: 9.8 GHz, microwave power: 0.2 mW, modulation amplitude: 5 G, field sweep: 200 and 1000 G) operating at room temperature. The pebbles were analysed in ER 221TUB/3 CFQ quality tubes with a diameter of 3 mm, both before and after irradiation. The reference marker ER 4119HS-2100 (g-factor: 1.9800 ± 0.0005, radical concentration: 1.15 · 10⁻³ %) was used for quantitative measurements.

The thermal stability and recombination of accumulated RD and RP were studied by TSL technique. The TSL glow emission, observed through a blue filter (a FIB002 of the Melles-Griot Company), was carried out using an automated Risø TL reader model TL DA-12 with an EMI 9635 QA photomultiplier. The reader is provided with a ⁹⁰Sr/⁹⁰Y beta source with a dose rate of 0.011 Gy s⁻¹ calibrated against a ¹³⁷Cs gamma source in a secondary standard laboratory. The samples were measured using a linear heating rate of 5 K s⁻¹ from room temperature up to 773 K in a nitrogen atmosphere. To acquire information about spectral distribution of TSL, another experimental setup was used: Andor Shamrock B-303i spectrograph equipped with a CCD camera Andor DU-401A-BV with different cryostats: from nitrogen cryostat to high-power

Table 2

Specification of irradiation conditions of the advanced and the reference Li₄ SiO₄ pebbles with 5 MeV accelerated electrons (D – absorbed dose, P – dose rate, T – irradiation temperature).

Sample	Description	D, MGy	P, MGy h ⁻¹	T _(cycle) , K	T _(aver.) , K	T _(min) , K	T _(max) , K
#0; #1; #2; #4	Un-treated	100	<10	(1) 850–930 (2) 1010–1120 (3) 770–900	920	770	1120
#0; #1; #2; #4	Thermally pre-treated	100	<10	(1) 580–640 (2) 700–770 (3) 820–840	710	580	840
#3	Un-treated	100	<10	(1) 790–950	730	500	950
#5	Thermally pre-treated			(2) 780–860 (3) 500–540			

heating element providing temperature range 8–700 K with variable heating rate (2 K s⁻¹ used).

The phase transitions and microstructural changes after irradiation were studied by p-XRD and SEM respectively. The p-XRD patterns were obtained by a Bruker D8 (range: 15–70° 2theta, scan speed: 0.02° 2theta, step time: 5 s, source: CuK α). The following datasets were used from the JCPDS PDF-2 (Release 2010) database: Li₄ SiO₄ – 074-0307, Li₂ SiO₃ – 029-0828 and Li₂ TiO₃ – 033-0831. The microstructure of the pebbles was examined at etched cross-sections with a field emission SEM (SUPRA 55, Zeiss).

The mechanical properties of the pebbles were analysed by performing compressive crush load tests before and after irradiation. 40 single monosized pebbles (diameter: 500 or 1000 μ m) were measured individually by a Zwick-Roell UTS electro-mechanical testing system. This method involves a continuously increasing load imposed onto single pebbles between sapphire plates until they break, after which the mean crush load was determined. Before the crush load test measurements, the pebbles were dried at 573 K for one hour in a nitrogen atmosphere to remove any moisture present.

3. Results and discussion

The un-treated and thermally pre-treated advanced Li₄ SiO₄ pebbles with additions of Li₂ TiO₃ as a secondary phase show an off-white colour – pale yellow, pink, purple or brown, before irradiation. During thermal pre-treatment slight changes from initial colour of the pebbles have been observed. It has been assumed that the colour might be caused by a redox reaction due to the presence of metallic impurities, added in the pebbles during the fabrication process or by the raw materials [9] associated, for example, with the reduction of Ti⁴⁺ ions or formation of oxygen vacancies during the fabrication process. Using p-XRD, it has been determined that the un-treated advanced pebbles have two main crystalline phases

– monoclinic Li₄ SiO₄ as the primary phase and monoclinic Li₂ TiO₃ as the secondary phase (Fig. 1). No traces of ternary compounds, such as, Li₂ TiSiO₅ [17], or chemisorption products, such as, lithium hydroxide (LiOH) or carbonate (Li₂ CO₃), were detected. After thermal pre-treatment, the diffraction peaks of Li₄ SiO₄ and Li₂ TiO₃ becomes higher and narrower, due to the increase in crystallinity.

In the advanced pebbles, both phases (Li₄ SiO₄ and Li₂ TiO₃) are fully separated [5] and it is anticipated that the mechanisms and the structure of the formed RD and RP during irradiation with 5 MeV accelerated electrons will be similar to single phase ceramics. Previously, the formation and accumulation of RD and RP in Li₄ SiO₄ and Li₂ TiO₃ ceramics under the action of neutron fluence, accelerated electrons and gamma rays have been investigated and described separately by several authors [18–25]. The formation and accumulation of RD and RP takes place through two stages: (1) fast generation of primary RD and RP on structural defects and impurities, and (2) slow generation due to the radiolysis of the basic matrix. As soon as the structural defects have been consumed, the

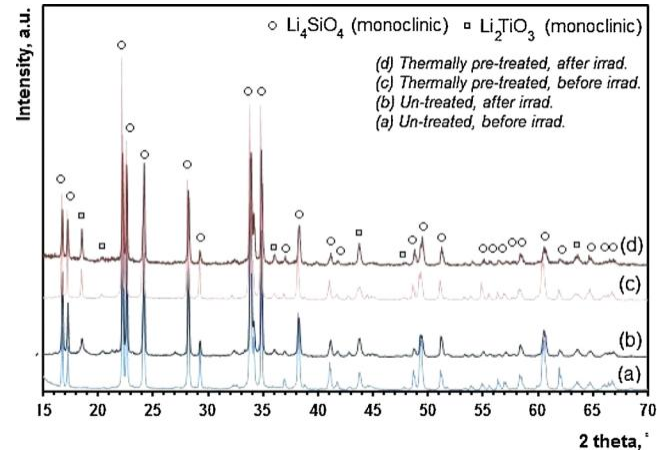


Fig. 1. p-XRD pattern of the un-treated and thermally pre-treated advanced Li₄ SiO₄ pebbles with 10 mol% Li₂ TiO₃ before and after irradiation with 5 MeV accelerated electrons up to 100 MGy absorbed dose at 500–1120 K in a dry argon atmosphere.

formation of RD and RP occurs only at the crystalline lattice. The thermal pre-treatment decreases the amount of structural defects, which may remain in the pebbles after the fabrication process, and thus it is anticipated that the thermally pre-treated pebbles will have higher radiation stability. Previously, the accumulated RD, such as, E' centres (SiO₃³⁻ and TiO₃³⁻), HC₂ centres (SiO₄³⁻ and TiO₃³⁻), peroxide radicals (\equiv Si O O \cdot) and Ti³⁺ centres, in the advanced pebbles were annihilated up to 650 K [6] and it has been expected, that during irradiation with temperatures higher than 500 K, the recombination processes of RD will dominate. Therefore, the formation of thermally stable RP is mainly expected, such as, colloidal lithium (Li_n) particles, elementary silicon (Si_n), molecular oxygen (O₂), silanol (\equiv Si Si \equiv), disilicate (\equiv Si O Si \equiv) and peroxide (\equiv Si O O Si \equiv) bonds.

After irradiation with 5 MeV accelerated electrons up to 100 MGy absorbed dose at 500–1120 K, a colour change of the advanced Li₄ SiO₄ pebbles was observed and the pebbles turned grey or black. Most likely, this effect is related to the formation and accumulation of optically active RD and RP, such as, F⁺ and F⁰⁰ centres (localised electrons in oxygen vacancies), Li_n particles etc. During irradiation at elevated temperatures, the radiolysis of the primary phase and the secondary phase can be expected to cause recrystallization and grain growth. However, major changes in the p-XRD patterns were not observed after irradiation (Fig. 1) and this effect could be related

to the small radiolysis degree (γ) of Li₄ SiO₄ ($1000\text{MGy} = 0.1\text{--}1\text{ mol\%}$ [18]) and Li₂ TiO₃ ($500\text{MGy} = 10^{-3}\text{ mol\%}$ [18]) and the detection limits of this method. The radiolysis degree is the percentage proportion of the decomposed molecules/ions versus the initial number of molecules/ions before irradiation. The detection limit of the p-XRD analysis depends on several factors (preferred orientation, texturing and particle size etc.), nevertheless, the detection

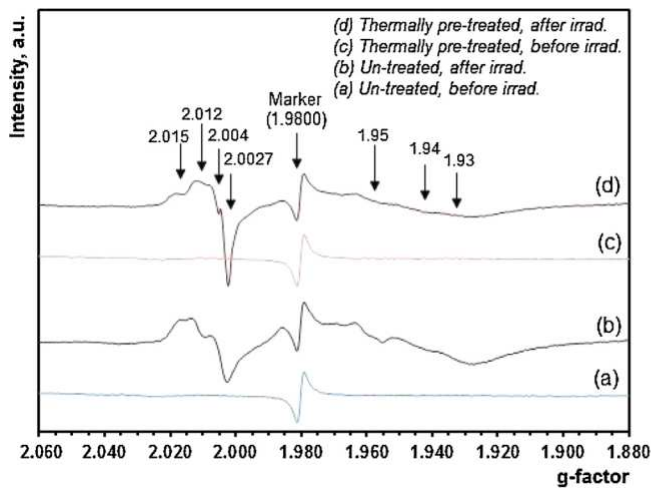


Fig. 2. ESR spectra of the un-treated and thermally pre-treated advanced Li_4SiO_4 pebbles with 10 mol% Li_2TiO_3 before and after irradiation with 5 MeV accelerated electrons up to 100 MGy absorbed dose at 500–1120 K in a dry argon atmosphere.

limit is typically around 0.1–1 wt.% for the samples with a mixed composition.

The ESR spectra of both the un-treated and thermally pre-treated advanced Li_4SiO_4 pebbles with 10 mol% Li_2TiO_3 before and after irradiation are shown in Fig. 2. In the ESR spectra, at least two groups of the first derivative signals were detected. The first group consists of four signals with g-factors from 2.015 to 2.002, while the second group of three signals is observed from 1.95 to 1.93. The signals of both groups have a similar shape, g-factor and linewidth to the signals, which were investigated and described in the single phase materials. Therefore, the ESR signals with a g-factor 2.012 ± 0.001 and 2.015 ± 0.001 were assigned to HC_2 centres (SiO_4^{3-} and TiO_3^-), while the signal with a g-factor of 2.004 ± 0.001 was attributed to E' centres (SiO_3^{3-} and TiO_3^{3-}). Presumably, the narrow ESR signal (singlet, $g = 2.0027$, $H < 0.2$ mT) could be associated with Li_n particles. The overlapping and wide signals with a g-factor from 1.95 to 1.93 might be associated to Ti^{3+} centres [26].

The E centres together with HC_2 centres are the primary stage electron and hole type RD, while Li_n particles (electron type RP) form in the second and third stage reactions of the radiolysis [19]. The Li_n particles form due to the aggregation of electron centers (F_n centers) and the following two kinds of particles may form – the fine particles with size < 1 m (Lorentz ESR line, $g = 2.0025$ and

$H < 10^{-2}$ mT [18]) and coarse particles with a size of 1–10 m (ESR singlet, $g = 2.0035$ and $H = 10$ mT [18]). Presumably, the signal of broad Li_n particles in the ESR spectra of the advanced pebbles cannot be observed due to overlapping with other signals. The accumulated RD and RP in single phase materials, Li_4SiO_4 and Li_2TiO_3 , are stable up to 700 K [12,13]. Therefore, due to the high irradiation temperature (500–1120 K), the concentration of the accumulated paramagnetic RD and RP in the advanced Li_4SiO_4 pebbles is quite small (around 10^{15} – 10^{18} defects g^{-1}). The total concentration of the accumulated RD and RP was calculated from the ESR results using a double integration method, and the results versus the content of Li_2TiO_3 are shown in Fig. 3. The irradiation temperature of the un-treated and thermally pre-treated Li_4SiO_4 pebbles with 0, 10, 20 and 30 mol% Li_2TiO_3 during the third irradiation cycle is comparable (range: 770–900 K) and thus these pebbles can be compared with each other. While, the detected concentration of paramagnetic RD and RP in the advanced pebbles with 25 and 40 mol% Li_2TiO_3 is slightly higher in comparison with other pebbles, most likely due to the smaller irradiation temperature in the last irradiation cycle (500–540 K), and thus these results were not included in Fig. 3.

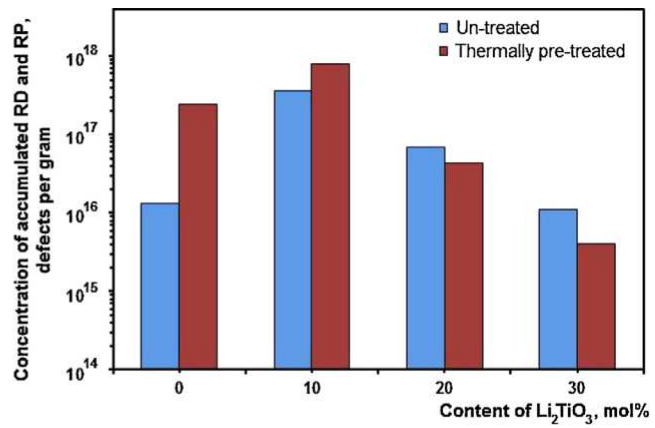


Fig. 3. The total concentration of accumulated paramagnetic RD and RP in the un-treated and thermally pre-treated Li_4SiO_4 pebbles with different contents of Li_2TiO_3 after irradiation with 5 MeV accelerated electrons up to 100 MGy absorbed dose at 500–1120 K in a dry argon atmosphere.

A previous irradiation study [6] already confirmed that the irradiation temperature has a significant impact on the formation and accumulation of paramagnetic RD and RP in the advanced Li_4SiO_4 pebbles. Therefore, the minor changes in the concentration of the accumulated RD and RP in the un-treated and thermally pre-treated pebbles could be attributed to the differences in the irradiation temperature. Nevertheless, Li_2TiO_3 has a smaller decomposition degree and radiation chemical yield of RD than Li_4SiO_4 [18], and thus with increasing content of Li_2TiO_3 as a secondary phase, the concentration of accumulated RD and RP in the advanced pebbles decreases. It has been assumed that the slight increase of accumulated RD and RP in the advanced pebbles with 10 mol% Li_2TiO_3 in comparison with the reference pebbles (0 mol% Li_2TiO_3) could be related to the structural defects (cracks, open and closed pores), which may form during the fabrication process due to the density differences between the liquid and the crystallised state.

To supplement the results of ESR spectrometry, the TSL glow curves and spectra of the advanced and the reference Li_4SiO_4 pebbles were measured. The thermally stimulated recombination of paramagnetic RD and RP in the advanced pebbles have been analysed in the previous research [6] and the correlation between results of the ESR spectrometry and the TSL technique have been detected. During heating, the luminescence emission occurs, due to the recombination reactions between various hole type RD and electron type RD and RP. The TSL glow curves of the pebbles (heating rate: 5 K s^{-1}) exhibit similar behaviour consisting of four peaks, three intense peaks at 450, 510 and 550 K and one weak maximum peaked in the range of 600–773 K regardless of the Li_2TiO_3 content (Fig. 4). Additionally, one can appreciate how the presence of Li_2TiO_3 practically do not affect to the shape of the TSL glow curves, number and position of peaks and therefore it has been assumed that similar hole-electron recombination processes occur in the advanced pebbles similar to the reference pebbles (0 mol% Li_2TiO_3). No signal was detected when measuring luminescence spectra with CCD camera and spectrometer in TSL peaks (heating rate: 2 K s^{-1}) as the intensity of emission was below the sensitivity limit of the detection system (TSL signal was observed only with photomultiplier tube connected directly). Previously, in the spectra of the reference pebbles at least two main bands with the maximum around 2.6–2.9 and 3.5–3.7 eV have been detected [24,27]. The luminescence band with the maximum around 2.6–2.9 eV most likely could be associated with E' centres (SiO_3^{3-}) [28], while the band with the maximum around 3.5–3.7 eV could be related to HC_2 centres (SiO_4^{3-}) [27].

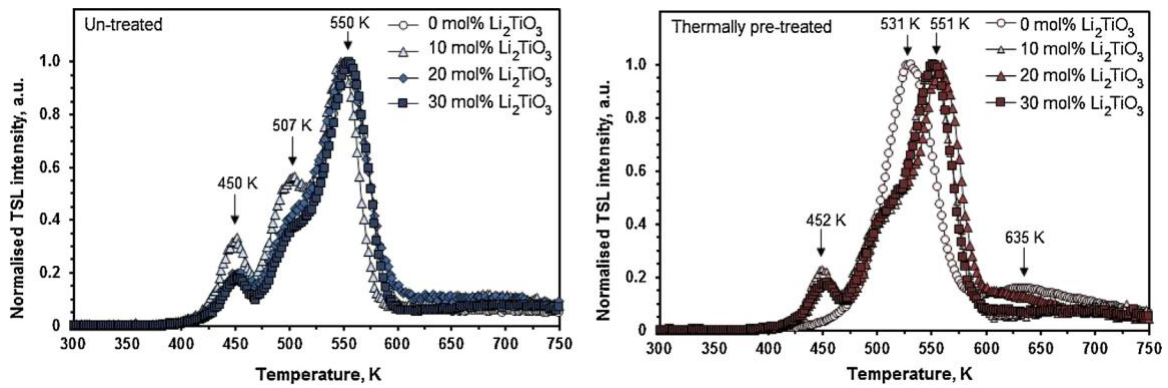


Fig. 4. Normalised TSL curves (heating rate: 5 K s^{-1}) of the un-treated and thermally treated Li_4SiO_4 pebbles with different contents of Li_2TiO_3 after irradiation with 5 MeV accelerated electrons up to 100 MGy absorbed dose at 500–1120 K in a dry argon atmosphere.

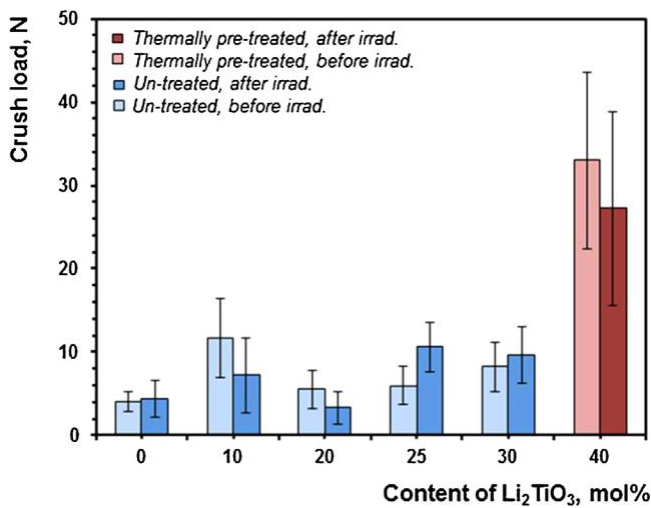


Fig. 5. Average crush load values of the Li_4SiO_4 pebbles with different contents of Li_2TiO_3 before and after irradiation with 5 MeV accelerated electrons up to 100 MGy absorbed dose at 500–1120 K in a dry argon atmosphere. The pebbles with 0, 20, 25 and 30 mol% of Li_2TiO_3 have a diameter of 500 m and the pebbles with 10 and 40 mol% of Li_2TiO_3 have a diameter of 1000 m.

The high-temperature radiolysis may cause changes to the microstructure of the advanced Li_4SiO_4 pebbles, due to the molecular oxygen evolution and the formation of micro-pores, cracks and dislocations. Therefore, to complement the results of p-XRD, ESR spectrometry and the TSL technique, the mechanical properties and the microstructure of the advanced Li_4SiO_4 pebbles before and after irradiation were studied by uniaxial compressive crush load tests and SEM, respectively. The crush load is dependent on the pebble size [29] and thus only mono-sized pebbles with diameters of 500 or 1000 m were analysed. 40 individual pebbles were used to determine the average crush load for each sample and the results for the Li_4SiO_4 pebbles with different contents of Li_2TiO_3 , both before and after irradiation, are shown in Fig. 5. The advanced pebbles with additions of 10 mol% and 40 mol% Li_2TiO_3 have a diameter 1000 m and thus, the average crush load values are generally larger. The large standard deviation of the results is very common for ceramics and can be attributed to small differences in the pebble microstructure including structural defects, minor variations in the pebble size or the composition, as well as different orientations between the sapphire plates during the compression test. It can therefore be said, that the crush load of the pebbles practically does not change after irradiation and the minor differences are within the limits of the standard deviation.

however, it is not excluded that these differences could partly also be attributed to the influence of various irradiation temperatures.

The microstructures of the Li_4SiO_4 pebbles with different contents of Li_2TiO_3 , which were analysed by SEM at etched cross-sections before and after irradiation, are shown in Fig. 6. The chemical compositions of the pebbles are given in the upper row. In the reference pebbles (0 mol% Li_2TiO_3), the dendritic Li_4SiO_4 phase is displayed in a dark grey colour with inclusions of light grey grains of Li_2SiO_3 . On the other hand, in the advanced pebbles with content up to 25 mol% Li_2TiO_3 , light grey grains of the secondary phase are very small and homogeneously distributed as inclusions between the Li_4SiO_4 dendrites, which appear dark-grey. For the advanced pebbles with 30 and 40 mol% Li_2TiO_3 , it can be seen that the lighter Li_2TiO_3 phase is the dominant crystal, taking a clear dendritic shape. In this case, the Li_4SiO_4 phase fills in the gaps between the Li_2TiO_3 dendrites, indicating a reverse in the crystallisation order. As expected from the results of the crush load test, the microstructure of the advanced pebbles after irradiation is only slightly changed. After irradiation, agglomeration of pores and cracking, due to the high irradiation temperature, can be seen. Nevertheless, it can be concluded that the advanced pebbles after irradiation maintain a microstructure comparable to the non-irradiated pebble.

On the basis of the obtained results, it can be concluded that the advanced Li_4SiO_4 pebbles with different contents of Li_2TiO_3 maintain a comparable radiation stability with the reference pebbles after the simultaneous action of 5 MeV accelerated electron beam (up to 10 MGy h^{-1}) and high temperature (up to 1120 K) in a dry argon atmosphere. The additions of Li_2TiO_3 as a secondary phase in the advanced Li_4SiO_4 pebbles does not provide new or different RD and RP, which could act as possible tritium scavenger centres, and thus it is expected that the tritium diffusion and release processes will be similar to single phase materials – Li_4SiO_4 pebbles and Li_2TiO_3 pebbles. The accumulated RD and RP annihilates around 423–773 K and thus it has been suggested that the main tritium release peaks could be expected in this temperature range. The pre-liminary deuterium and tritium release studies [7,30] confirm these assumptions, however additional research on the tritium release from the advanced pebbles is required to evaluate the applicability of the breeder pebbles.

4. Conclusion

The advanced Li_4SiO_4 pebbles with different contents of Li_2TiO_3 were examined before and after the simultaneous action of 5 MeV accelerated electron beam (dose rate: up to 10 MGy h^{-1}) and high

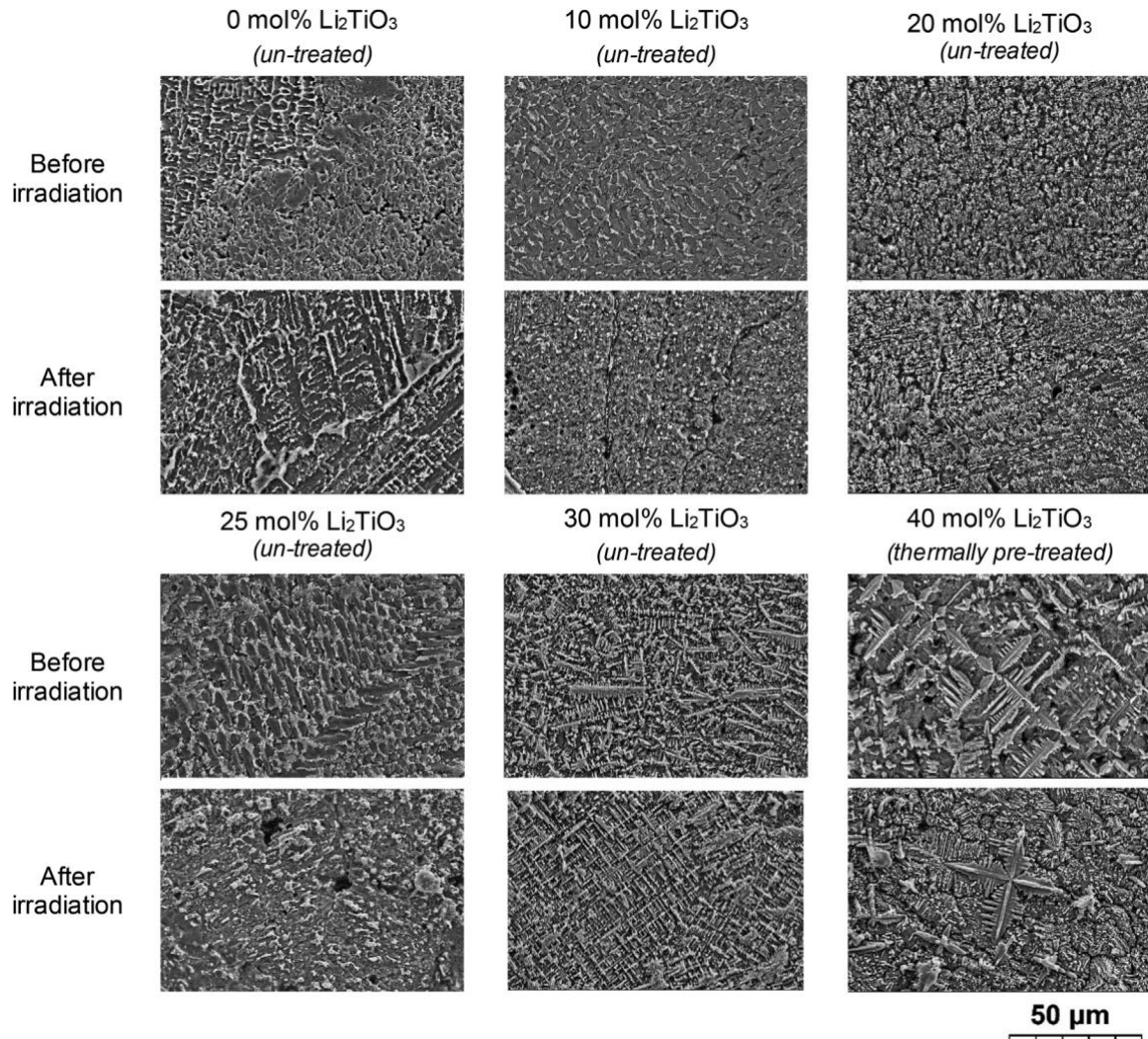


Fig. 6. SEM images of the Li_4SiO_4 pebbles with different contents of Li_2TiO_3 before and after irradiation with 5 MeV accelerated electrons up to 100 MGy absorbed dose at 500–1120 K in a dry argon atmosphere.

temperature (up to 1120 K) in a dry argon atmosphere. During the irradiation of the advanced Li_4SiO_4 pebbles, the recombination processes of RD dominated and the thermally stable RP were mainly accumulated. ESR spectrometry corroborates that in the advanced pebbles, several paramagnetic RD and RP, which are similar to single phase ceramics, are accumulated, namely, E' centres (SiO_3^{3-} and TiO_3^{3-}), HC_2 centres (SiO_4^{3-} and TiO_3^-), Li_n particles and Ti^{3+} centres. As well as the irradiation temperature that has a significant impact on the formation of RD and RP, and with an increasing content of Li_2TiO_3 , the concentration of accumulated paramagnetic RD and RP decreases. The TSL technique confirmed that the accumulated RD and RP recombine around 423–773 K. Major changes in the mechanical properties, microstructure and phase composition were not detected after irradiation.

Acknowledgements

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