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

A. Zarins[a,b,*], O. Leys[c], G. Kizane[a], A. Supe[a], L. Baumane[a,d], M. Gonzalez[e], V. Correcher[e], C. Boronat[e], A. Zolotarjovs[f], R. Knitter[c]

[a] University of Latvia, Institute of Chemical Physics, Jelgavas street 1, LV-1004, Riga, Latvia
[b] Daugavpils University, Faculty of Natural Science and Mathematics, Department of Chemistry and Geography, Parades street 1a, Daugavpils, LV-5401, Latvia
[c] Karlsruhe Institute of Technology, Institute for Applied Materials (IAM-KWT), 76021, Karlsruhe, Germany
[d] Latvian Institute of Organic Synthesis, Aizkraukles street 21, LV-1006, Riga, Latvia
[e] LNF-CIEMAT, Materials for Fusion Group, Av. Complutense 40, 28040, Madrid, Spain
[f] University of Latvia, Institute of Solid State Physics, Kengaraga street 8, LV-1063, Riga, Latvia

HIGHLIGHTS

- Irradiation temperature affects accumulation of radiation-induced defects (RD) and radiolysis products (RP).
- With an increasing content of Li_2TO_3 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.

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ABSTRACT

Advanced lithium orthosilicate (Li_4SiO_4) pebbles with additions of lithium metatitanate (Li_2TiO_3) as a secondary phase are suggested as a potential source for tritium breeding in future nuclear fusion reactors. The advanced Li_4SiO_4 pebbles with different contents of Li_2TiO_3 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 Li_4SiO_4 pebbles, and with an increasing content of Li_2TiO_3, 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 (Li_4SiO_4) and lithium metatitanate (Li_2TiO_3) 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 10^{18} 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 Li_4SiO_4 pebbles need to be improved, while Li_2TiO_3 pebbles require a higher enrichment with lithium-6, to increase tritium production.

* Corresponding author at: University of Latvia, Institute of Chemical Physics, Jelgavas street 1, LV-1004, Riga, Latvia.
E-mail address: arturs.zarins@lu.lv (A. Zarins).

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Table 1
Specification of the investigated advanced Li_4SiO_4 pebbles with different contents of Li_2TiO_3 and the reference pebbles.

Sample	Pebbles	Phase compositions			Pebble size (μm)	Description
		Li_4SiO_4, mol%	Li_2TiO_3, mol%	Li_2SiO_3, mol%		
#0	Reference	90	0	10	500	Un-treated
					650–900	Thermally pre-treated
#1	Advanced	90	10	0	1000	Un-treated
					650–900	Thermally pre-treated
#2	Advanced	80	20	0	500	Un-treated
					650–900	Thermally pre-treated
#3	Advanced	75	25	0	500	Un-treated
#4	Advanced	70	30	0	500	Un-treated
					650–900	Thermally pre-treated
#5	Advanced	60	40	0	1000	Thermally pre-treated

The advanced Li_4SiO_4 pebbles with additions of Li_2TiO_3 as a secondary phase have been proposed as an alternative candidate for the tritium breeding [4]. The optimum content of Li_2TiO_3 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 Li_4SiO_4 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 Li_4SiO_4 pebbles with various contents of Li_2TiO_3 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 Li_4SiO_4 pebbles with five different contents of Li_2TiO_3 were selected for this research together with the reference pebbles (Table 1). The reference pebbles (0 mol% Li_2TiO_3) consist of two main phases – Li_4SiO_4 as the primary and lithium metasilicate (Li_2SiO_3) as a secondary phase, and they are the present reference material for tritium breeding in the EU developed concept [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 Li_4SiO_4 pebbles with different contents of Li_2TiO_3 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: $1.15 \cdot 10^{-3}$ %) 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 $^{90}Sr/^{90}Y$ beta source with a dose rate of 0.011 Gy s^{-1} calibrated against a ^{137}Cs 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