

Formation and accumulation of radiation-induced defects and radiolysis products in modified lithium orthosilicate pebbles with additions of titanium dioxide



Arturs Zarins^{a, b, *}, Oskars Valtenbergs^{a, b}, Gunta Kizane^a, Arnis Supe^a, Regina Knitter^c, Matthias H.H. Kolb^c, Oliver Leys^c, Larisa Baumane^{a, d}, Davis Conka^{a, b}

^a University of Latvia, Institute of Chemical Physics, Jelgavas Street 1, LV-1004, Riga, Latvia

^b University of Latvia, Faculty of Chemistry, Jelgavas Street 1, LV-1004, Riga, 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

H I G H L I G H T S

- Formation of RD and RP in modified Li_4SiO_4 pebbles with additions of TiO_2 is analysed for the first time.
- Due to additions of TiO_2 , concentration of paramagnetic RD slightly increased in modified Li_4SiO_4 pebbles.
- Modified Li_4SiO_4 pebbles have good radiation stability compared to reference pebbles.
- Irradiation temperature has significant impact on radiolysis of modified Li_4SiO_4 pebbles.

A R T I C L E I N F O

Article history:

Received 3 June 2015

Received in revised form

21 December 2015

Accepted 22 December 2015

Available online 24 December 2015

Keywords:

Tritium breeding ceramic

Lithium orthosilicate

Radiolysis

Accelerated electrons

Irradiation temperature

A B S T R A C T

Lithium orthosilicate (Li_4SiO_4) pebbles with 2.5 wt.% excess of silicon dioxide (SiO_2) are the European Union's designated reference tritium breeding ceramics for the Helium Cooled Pebble Bed (HCPB) Test Blanket Module (TBM). However, the latest irradiation experiments showed that the reference Li_4SiO_4 pebbles may crack and form fragments under operation conditions as expected in the HCPB TBM. Therefore, it has been suggested to change the chemical composition of the reference Li_4SiO_4 pebbles and to add titanium dioxide (TiO_2), to obtain lithium metatitanate (Li_2TiO_3) as a second phase. The aim of this research was to investigate the formation and accumulation of radiation-induced defects (RD) and radiolysis products (RP) in the modified Li_4SiO_4 pebbles with different contents of TiO_2 for the first time, in order to estimate and compare radiation stability. The reference and the modified Li_4SiO_4 pebbles were irradiated with accelerated electrons ($E = 5 \text{ MeV}$) up to 5000 MGy absorbed dose at 300–990 K in a dry argon atmosphere. By using electron spin resonance (ESR) spectroscopy it was determined that in the modified Li_4SiO_4 pebbles, several paramagnetic RD and RP are formed and accumulated, like, E' centres ($\text{SiO}_3^{\cdot-}/\text{TiO}_3^{\cdot-}$), HC_2 centres ($\text{SiO}_4^{\cdot-}/\text{TiO}_3$) etc. On the basis of the obtained results, it is concluded that the modified Li_4SiO_4 pebbles with TiO_2 additions have comparable radiation stability with the reference pebbles.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In the International Thermonuclear Experimental Reactor (ITER, Cadarache, France) several concepts of Test Blanket Modules

(TBMs) will be tested and verified, because the tritium breeding is a key issue in future burning plasma machines, like, DEMO (Demonstration fusion power plant) [1–5]. The Helium Cooled Pebble Bed (HCPB) TBM, proposed by the European Union, will use lithium orthosilicate (Li_4SiO_4) pebbles with 2.5 wt% excess of silicon dioxide (SiO_2) as the reference tritium breeding ceramic [4–7]. Due to the excess of SiO_2 , the reference pebbles have two phases – 90 mol% Li_4SiO_4 and 10 mol% lithium metasilicate (Li_2SiO_3) [8–10].

* Corresponding author. University of Latvia, Institute of Chemical Physics, Jelgavas Street 1, LV-1004, Riga, Latvia.

E-mail address: arturs.zarins@lu.lv (A. Zarins).

The reference Li_4SiO_4 pebbles with 2.5 wt% excess of SiO_2 have appropriate properties for the tritium breeding, i.e. a high lithium density (up to 0.54 g cm^{-3}) and melting point (eutectic point at 1298 K), a good tritium release behaviour and chemical compatibility with structural materials, i.e. Eurofer steel [6,7]. However, beside the main task to produce and release tritium, the reference pebbles must also be able to withstand the harsh conditions as expected during exploitation.

The tritium breeding ceramic in the HCPB TBM will be simultaneously exposed to an intense neutron flux (up to $10^{18} \text{ neutrons m}^{-2} \text{ s}^{-1}$), ionizing radiation dose rate (up to 1 kGy s^{-1}), a high magnetic field (7–10 T) and elevated temperatures (570–1190 K) [1,5,11,12].

The latest neutron irradiation experiments [13] showed that the reference Li_4SiO_4 pebbles will likely perform sufficiently well in the HCPB TBM. However, it has also been reported that the reference pebbles may crack and form fragments during irradiation. Therefore, it has been suggested to increase the mechanical stability of the reference pebbles, so that the pebbles withstand the operation conditions as expected in the HCPB TBM.

One possible option to increase the mechanical stability of the tritium breeding ceramic is to change the chemical composition of the reference Li_4SiO_4 pebbles by adding titanium dioxide (TiO_2) [6,7]. Due to the additions of TiO_2 , lithium metatitanate (Li_2TiO_3) is obtained as a secondary phase in the modified Li_4SiO_4 pebbles. Li_2TiO_3 pebbles are also approved as a “back-up” solution for the tritium breeding in the HCPB TBM, due to the good tritium release behaviour and appropriate mechanical, thermal and chemical properties [4–7,13,14]. Therefore, in combining these two phases – Li_4SiO_4 and Li_2TiO_3 – it is anticipated to obtain a modified tritium breeding ceramic with improved mechanical properties, without losing the benefit of the high lithium density, melting temperature and good tritium release behaviour.

However, to develop a new chemical composition for the tritium breeding ceramic, it is a critical issue to understand the physico-chemical processes (e.g. radiolysis), phase transitions and micro-structural changes, which will occur during irradiation. From previous studies [15–17], it is known that the formation, accumulation and annihilation of radiation-induced defects (RD) and radiolysis products (RP) may occur in the ceramic during irradiation. Such RD and RP will induce changes of thermal and mechanical properties, swelling and degradation of mechanical integrity, and may also affect the tritium diffusion and release process [15–34].

The aim of this research was to investigate the formation and accumulation of RD and RP in the modified Li_4SiO_4 pebbles with different TiO_2 contents for the first time, in order to estimate and compare the radiation stability.

2. Literature review

For now, the modified Li_4SiO_4 pebbles with additions of TiO_2 have only been investigated by a few groups of researchers and thus there is a gap in the theoretical and practical knowledge about this ceramic. The first articles about the fabrication and development of the modified pebbles were published by R. Knitter et al. [7] and O. Leys et al. [35]. It was found that the additions of TiO_2 in the Li_4SiO_4 pebbles significantly increased the crush load, while the closed porosity slightly increased with increasing the content of TiO_2 .

D. A.H. Hanaor et al. [36] made a behavioural phase transformation diagram of the quasi-binary Li_4SiO_4 – Li_2TiO_3 system, to understand the phase stability and melting of the modified Li_4SiO_4 pebbles. It was reported that the mixed phase material shows liquid formation from the melting of the Li_4SiO_4 phase at temperatures $>1373 \text{ K}$.

M. Gonzalez et al. [37] investigated the influence of the radiation-induced processes on the sorption and desorption of deuterium (D_2) in the modified Li_4SiO_4 pebbles. It was shown that the mechanisms of D_2 desorption in the modified pebbles highly depends on the radiation-induced effects.

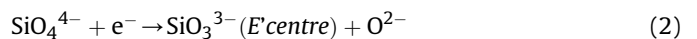
However, until now, the radiolysis of the modified Li_4SiO_4 pebbles was not analysed, and thus additional research is required, to understand the formation, accumulation and annihilation of RD and RP during irradiation at elevated temperature. Previously, the radiolysis of the reference Li_4SiO_4 pebbles and the Li_2TiO_3 pebbles have been investigated separately.

2.1. Radiolysis of the reference Li_4SiO_4 pebbles with excess of SiO_2

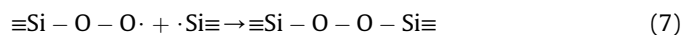
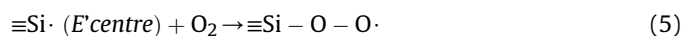
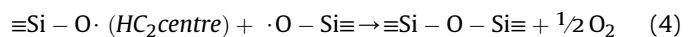
The reference Li_4SiO_4 pebbles with excess of SiO_2 have two crystalline phases – Li_4SiO_4 as the primary phase and Li_2SiO_3 as a secondary phase. The radiolysis of the Li_4SiO_4 ceramic and the Li_2SiO_3 ceramic have been analysed and described by several authors [15–25]. Both, Li_4SiO_4 and Li_2SiO_3 have chemical bonds [$\equiv\text{Si}-\text{O}^- \text{Li}^+$] and thus the mechanisms of the radiolysis and the structure of the formed RD and RP will be similar in both cases. Therefore, the radiolysis of a secondary phase, Li_2SiO_3 , in the reference pebbles will not be discussed separately in this research.

The mechanism of the radiolysis is the same for the Li_4SiO_4 powders, pebbles, pellets and other ceramics; only the quantitative parameters of the radiolysis are different [25]. The localisation of RD and RP takes place through two stages. In the first stage, primary RD and RP localise mainly on structural defects and impurities, while in the second stage, the radiolysis of the matrix occurs. At the second stage in bulk ceramics (pebbles, pellets etc.), the formation of RD and RP proceeds slowly in comparison with the powders. Therefore, dense ceramic materials usually have higher radiation stability in comparison with powders.

A. Abramenkovs et al. [16] and J. Tiliks et al. [15,17,25] reported that the radiolysis of the reference Li_4SiO_4 pebbles can be divided into three main stages. In the first stage, primary electron and hole type RD, like, E' centres ($\equiv\text{Si}\cdot$ or SiO_3^{3-}) and HC_2 centres ($\equiv\text{Si}-\text{O}\cdot$ or SiO_4^{4-}), are formed (Eqs. (1) and (2)). The symbol “ \equiv ” represents three bonds to three oxygen atoms in the crystal structure.



In the second stage of the radiolysis, secondary RD, like peroxide radicals ($\equiv\text{Si}-\text{O}-\text{O}\cdot$) and chemically stable molecular compounds – RP, are generated (Eqs. (3)–(7)). The major RP are colloidal lithium (Li_n), elementary silicon (Si_n), molecular oxygen (O_2), silanol ($\equiv\text{Si}-\text{Si}\equiv$), disilicate ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) and peroxide ($\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$) bonds.



In the third and final stage of the radiolysis, chemical reactions between RP proceed and chemical compounds, for example lithium oxide (Li_2O), are formed.

Download English Version:

<https://daneshyari.com/en/article/7964679>

Download Persian Version:

<https://daneshyari.com/article/7964679>

[Daneshyari.com](https://daneshyari.com)