Scientific Journal of Riga Technical University
Material Science and Applied Chemistry
2010
Volume 22

Radiolysis of Slightly Overstoichiometric Lithium Orthosilicate Pebbles

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Abstract: **One of the technological problems of a fusion reactor is the change in composition and structure of ceramic breeder (Li_4SiO_4 or Li_2TiO_3 pebbles) during long-term operation. Changes in the composition and structure of the Li_4SiO_4 ceramic pebbles at fast electron irradiation (E = 5 MeV, dose rate up to 88 MGy•h^{-1}, absorbed dose up to 10.6 GGy) at 543-573 K were investigated in this study.**

Overstoichiometric (2.5 weight % of additional SiO_2) lithium orthosilicate pebbles were fabricated by a melt-spraying process (Schott AG, Mainz, Germany). Three types of pebbles with different annealing time, diameter and grain size were investigated: pebbles annealed at 1073 K 1h (diameter <50 µm, grain size 1 µm), annealed at 1173 K 128 h (diameter <50 µm, grain size 8 µm) and pebbles annealed at 1243 K 168 h diameter 500 µm, grain size 10µm). Products of radiolysis were investigated by means of FTIR and XRD, TSL and ESR spectroscopy were used for detection of radiation defects.

Additional phases were observed in the small pebbles after the irradiation up to 10.6 GGy by means of FTIR and XRD methods. The traces of LiOH, Li_2CO_3, Li_2SiO_3 and $Li_6Si_2O_7$ were identified. The lines of SiO_4^{3-} (HC2) and SiO_3^{3-}(E') ion radicals were observed in ESR spectra for all three samples, but F^+ centres was observed only in ESR spectra of pebbles annealed at 1073 K 1h. For all three types of pebbles four maxima were observed in TSL glow curves, but in the optical spectra wide band at 3.5 eV. Comparison of obtained date for investigated pebbles allow to say that the sample #3 (pebbles annealed at 1243 K 168 h with diameters of 500 µm and a grain size of 10µm) have higher radiation stability as the other two.

Keywords: **lithium orthosilicate, radiolysis, ceramic pebbles**

I. Introduction

Slightly overstoichiometric lithium orthosilicate (Li_4, SiO_4) pebbles with diameters ranging from 250 to 630 µm have been selected as one possible breeder material for the European Helium Cooled Pebble Bed blanket. Under operating conditions of a fusion reactor, the blanket materials will be at high temperature (up to 1123 K), under action of high magnetic field (up to 10 T) and intense radiation (up to 10^{19} neutrons·m^{-1}·s^{-1}). One of the technological problems of a fusion reactor is the change in composition and structure of ceramic breeder (Li_4SiO_4 or Li_2TiO_3 pebbles) during long-term operation. Changes in the composition and structure of the Li_4SiO_4 ceramic pebbles at fast electron irradiation up to absorbed dose 10.6 GGy at 270-300 °C were investigated in this study.

Lithium orthosilicate pebbles are fabricated by a melt-spraying method in a semi-industrial scale facility [1, 2] at Schott AG, Mainz, Germany. While larger pebbles crystallize during cooling, pebbles with diameters <50 µm solidify amorphously. For the experiments, pebbles <50 µm were heat treated at different temperatures to achieve crystallization and microstructure with different mean grain sizes. Additionally, already crystallized pebbles (500 µm) were annealed to obtain a homogeneous microstructure. Characteristics of investigated samples of slightly overstoichiometric lithium orthosilicate pebbles are summarised in Table 1.

Unfortunately, an admixture of Li_2SiO_3 in overstoichiometric Li_4SiO_4 can increase the concentration of oxygen vacancies causing decrease of radiation stability. Therefore production of radiation defects and products of radiolysis were investigated. The pebbles were irradiated in quartz tubes in both air and dry argon atmosphere with accelerated 5 MeV electrons at 983 K by means of ELU4 accelerator (Salaspils, Latvia). The dose rate of 24444 Gy/s was calculated from measured electron flux by means of ionization chamber and Faraday cylinder.

ESR spectra of the radiation-induced free radicals where recorded on a Bruker BioSpin X-band radiospectrometer operating at 100 kHz field modulation. X-ray diffraction were measured on a Bruker D8 Advanced XRD spectrometer (source: CuKα, λ=0.15418 nm). Fourier transform infrared spectroscopy (FTIR) was performed by means of AVATAR 330 FTIR Thermo Nicolet and BRUKER EQUINOX55 spectrometers. Thermally stimulated luminescence (TSL) was measured at a heating rate 2 K/s.

TABLE 1

OVERVIEW OF THE INVESTIGATED PEBBLES

Nr.	Pebble size, µm	Grain size, µm	Annealing temperature, K	Annealing time, s	Conc. of SiO_2, wt.%
#1	<50	1	1073	3600	2.5
#2	<50	8	1173	460800	2.5
#3	455 ±5	10	1243	604800	2.5

II. Results and discussion

EPR spectra of all investigated samples after irradiation with doses up to 10.58 GGy showed presence of at least 3 different lines with g-factors 2.001, 2.016 and 2.018. Those spectra were similar to previously reported ones for irradiated "pure" Li_4SiO_4 [3] and can be interpreted as superposition of signals from so called E' and HC2 centres (ion radicals SiO_3^{3-} and SiO_4^{3-}, respectively). Very week and board multiplex signal was also observed at ESR spectra of irradiated sample #1. This signal can be attributed to electron localised in anion or oxygen vacancy (so called F^+ centres). ESR spectra of all three samples irradiated in air atmosphere with dose 10.56 GGy contain two symmetric lines with 50.2 mT splitting, typical for localised hydrogen atoms. Concentration of stabilised paramagnetic centres in pebbles irradiated with doses from 1 to 5 GGy are in range 10^{15}-10^{16} radical/g and slightly increase with increasing absorbed dose. Surprising high concentration of stabilised paramagnetic centres ($10^{17}÷10^{19}$ radical/g) was observed in samples irradiated with dose 10.56 GGy in air atmosphere (see Table 2). Concentration of free radicals stabilised in samples irradiated in dry argon atmosphere were significantly higher than in case of samples irradiated in air atmosphere and decrease with increasing absorbed dose up to 5 GGy.

TABLE 2
Characteristics of ESR spectra

Sample	Irradiation	Radical	g-factor	Splitting, mT	Concentration, 10^{18} radicals/g
#1	accelerated electrons, air atmosphere, 1.32 GGy	E' HC2 F^+	2.0013 2.0100 2.0022	none none unresolved	0.00002 0.00080 0.00009
#1	accelerated electrons, air atmosphere, 2.64 GGy	E' HC2	2.002 2.009	none none	0.0003 0.0007
#1	accelerated electrons, air atmosphere, 5.28 GGy	E' HC2	2.00 2.01	none none	0.0009 0.0007
#1	accelerated electrons, air atmosphere, 10.56 GGy	E' HC2 H	2.0011 2.0154 2.0023	none none 50.2	22.5 0.05 0.01
#2	accelerated electrons, air atmosphere, 1.32 GGy	E' F^+	2.0018 2.0022	none unresolved	0.0002 0.0001
#2	accelerated electrons, air atmosphere, 2.64 GGy	E'	2.00	none	0.005
#2	accelerated electrons, air atmosphere, 5.28 GGy	E' HC2	2.001 2.012	none none	0.025 0.001
#2	accelerated electrons, air atmosphere, 10.56 GGy	E' HC2 H	2.001 2.006 2.002	none none 50.2	0.065 0.004 0.001
#3	accelerated electrons, air atmosphere, 10.56 GGy	E' HC2	2.00 2.01	none none	0.0009 0.0001
#3	accelerated electrons, air atmosphere, 2.64 GGy	E'	2.00	none	0.0003
#3	accelerated electrons, air atmosphere, 5.28 GGy	E' HC2	2.00 2.01	none none	0.0039 0.0002
#3	accelerated electrons, air atmosphere, 10.56 GGy	E' HC2 H	2.00 2.01 2.00	none none 50.2	0.39 0.12 0.01

TSL curves of irradiated pebbles were also similar to previously reported ones for irradiated "pure" Li_4SiO_4 [3] and contain three maxima at temperatures 395 ±25, 438 ±12 and 500 ±50. In high temperature region the fourth maximum at 612 ±38 K were observed (see Fig. 1). Maximum at 500 ±50 K is unstable and disappears in 60 days after irradiation.

TSL intensity of samples irradiated in dry argon atmosphere is significantly higher than in case of samples irradiated in air atmosphere. In TSL curves of pebbles irradiated in argon atmosphere predominates the maximum at high temperature region (612 ±38 K).

TSL optical spectra of all investigated samples indicate maximum at 3.5 eV. Only TSL optical spectra of pebbles irradiated with a dose less than 1 GGy have a maximum at 2.9 eV. Both these maxima have previously been observed in TSL and radioluminescence spectra of "pure" Li_4SiO_4 [3]. The Luminescence band with the maximum at 3.5 eV is due to exited states of SiO_4^{4-} anions (so called "L-centres", [3]). The origin of luminescence band with a maximum at 2.9 eV is not clear yet, but we think that it is due to excited state of electrons localised in structure defects (so called "F^+-centres"). Light absorption spectra registered by means of light diffuse refraction spectroscopy have a maximum at 3.0 eV (415 nm). So small shifts (approximately 0.1 eV) between maxims of light absorption and emission bands of F-centres were observed in case of irradiated alkali metal sulphates [4].

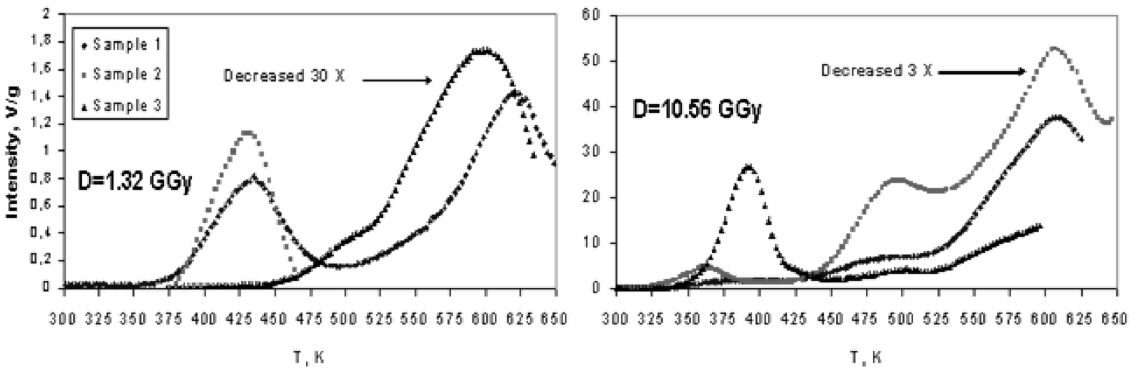

Fig.1. TSL curves of lithium orthosilicate pebbles after irradiation with doses 1.32 and 10.56 GGy (numbering of investigated samples according Table 1)

TABLE 3
RELATION OF INTENSITIES OF CHARACTERISTIC XRD LINES (10.58 GGY/UNIRRADIATED)

Compound	2θ of characteristic lines	Relation of intensities $I_{10.58}/I_0$		
		Sample #1	Sample #2	Sample #3
Li_4SiO_4	22.6 24.2 28.2	0.9 0.3 0.2	0.8 0.4 0.1	0.7 0.6 0.6
Li_2SiO_3	18.9 27.0 33.2	1.1 1.8 1.4	1.7 1.5 1.6	1.5 1.4 1.5
Li_2CO_3	29.5 31.8 35.6	1.8 2.2 1.8	1.6 1.6 2.6	3.3 5.0 3.0
LiOH	17.5 35.4	1.6 1.9	1.9 1.6	5.0 5.5
$Li_6Si_2O_7$	25.6	1.9	1.6	5.0

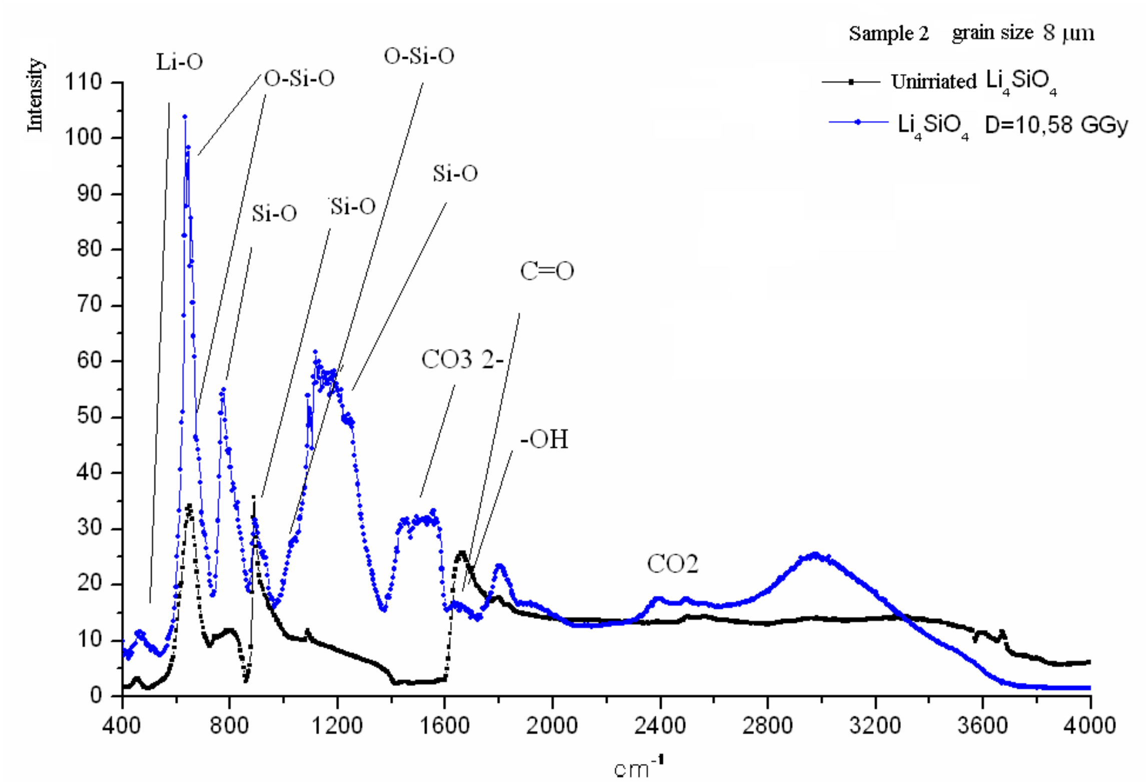

Fig.2. FTIR spectra of unirradiated and irradiated (10.56 GGy, in air) lithium orthosilicate (sample #2, grain size 8 μm)

Thus, in irradiated pebbles the same radiation defects are stabilized, which have been detected in “pure” Li_4SiO_4, but the concentration of stabilized free radicals at doses from 1 to 5 GGy is approximately 2 times higher (ESR measurements of “pure” Li_4SiO_4 irradiated with a dose of 10.56 GGy have not been made previously).

Products of radiolysis in irradiated pebbles were investigated by means of XRD and FTIR spectroscopy. Significant increase (at least by 50 %) of the initial concentration of Li_2SiO_3 was found by means of both mentioned methods. Beside this, in XRD spectra of irradiated (dose 10.56 GGy) pebbles lines due to $Li_6Si_2O_7$ were observed. On the other hand, intensities of Li_4SiO_4 characteristic lines decrease with increasing absorbed dose (see Table 3).

In samples irradiated in air atmosphere, characteristic lines for LiOH and Li_2CO_3 were detected with both mentioned methods (see Table 3 and Fig. 2).

Unfortunately it was impossible to determine concentration of products of radiolysis by means of XRD and FTIR spectroscopy. As can be seen from Table 2 in case of sample #3 irradiated with a dose of 10.58 GGy ratios of intensities of lines from LiOH and Li_2CO_3 versus intensities of the same lines in XRD spectra of unirradiated sample #3 are approximately two times higher than in case of samples #1 and #2. This is due to the fact that concentration of LiOH and Li_2CO_3 impurities in unirradiated sample #3 is significantly lower than in samples #1 and #2, but concentration of LiOH and Li_2CO_3 in all three samples irradiated with dose 10.58 GGy is approximately equal. Concentration of Li_2SiO_3 formed in a process of radiolysis is approximately 1% of weight or 4 molar % in all three samples irradiated with dose 10.58 GGy.

Reported results are in a good agreement with assumption that radiolysis of Li_4SiO_4 can be described with a following summary equation:

$$Li_4SiO_4 \rightsquigarrow 2Li + Li_2SiO_3 + 1/2O_2$$

In the air atmosphere colloidal lithium reacts with oxygen, moisture and carbon dioxide forming Li_2O, LiOH and Li_2CO_3. We think that atomic hydrogen (identified by means of ESR spectroscopy) is product of LiOH radiolysis.

In conclusion it should be noted that degree of decomposition of lithium orthosilicate matrix at absorbed dose 10.58 GGy $\alpha_{10.58}$ calculated form estimated concentration of radiolytic metasilicate is approximately equal to 1.5%. It is significantly lower, than value $\alpha_{10.58} \approx 10\%$ extrapolated from previously reported degree of decomposition of "pure" Li_4SiO_4 at dose 0.04 GGy $\alpha_{0.04} = 0.43\%$ [5]. Comparison of obtained data for investigated pebbles allow to say that the sample #3 (pebbles annealed at 1243 K for 168 h with diameters of 500 µm and with grain size 10 µm) have higher radiation stability as others two.

ACKNOWLEDGEMENTS

This study was carried out with support of the Ministry of Education and Science in the frame of State Investigation Programme “Materialscience” and in collaboration with Karlsruhe Institute of Technology, Institute for Materials Research III, Germany

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Artūrs Zarins, Arnis Supe, Gunta Kizane, Regīna Knitter, Ingars Reinholds, Aigars Vitins, Vija Tilika, Andris Actins, Nestehiometrisku litija ortosilikāta lodīšu radiolīze

Viena no kodolsintēzes reaktoru tehnoloģijas galvenajām problēmām ir litiju saturošo tritiju atražojošo materiālu (Li_4SiO_4 vai Li_2TiO_3) sastāva un struktūras izmaiņas ilgstošas ekspluatācijas gaitā. Šī darba mērķis bija izpētīt Li_4SiO_4 keramikas lodīšu sastāva un struktūras izmaiņas paātrināto elektronu starojuma (E = 5 MeV, dozas jauda līdz 88 MGy•h^{-1}, absorbētā doza līdz 10,6 GGy) iedarbības rezultātā 542-570 K temperatūrā.

Ar kausējuma izsmidzināšanas metodi tika iegūtas trīs dažādu tipu nestehiometriskas (ar 2,5 masas % SiO_2 pārpalikumu) litija ortosilikāta keramikas lodītes (Schott AG, Mainz, Vācija): lodītes ar diametru līdz 50 µm un grauda izmēru 1 µm (atdedzinātas 1 stundu līdz 1073 K), lodītes ar diametru līdz 50 µm un grauda izmēru 8 µm (atdedzinātas 128 stundas līdz 1173 K) un lodītes ar diametru no 450 µm līdz 560 µm un grauda izmēru 10 µm (atdedzinātas 168 stundas līdz 1243 K). Radiolīzes produktu noteikšanai tika izmantota Furjē spektroskopija un rentgenstruktūranalīze, bet radiācijas defekti tika pētīti ar elektronu paramagnētiskās rezonanses (EPR) un termostimulētās luminiscences (TSL) metodēm.

Ar Furjē spektroskopijas un rentgenstruktūranalīzes metodēm tika konstatēta jaunu fāzu veidošanās līdz 10,56 GGy apstarotās lodītēs. Tika konstatēta LiOH, Li_2CO_3, Li_2SiO_3 un $Li_6Si_2O_7$ veidošanās. Apstarotu lodīšu EPR spektros tika novērotas jonradikāliem SiO_4^{3-} (HC2) un SiO_3^{3-} (E') atbilstošas līnijas, bet F^+ centri tika novēroti tikai 1073 K 1stundu atdedzināto lodīšu spektros. Visu 3 lodīšu veidu TSL līknēs tika novēroti 4 maksimumi, bet TSL optiskajos spektros ir redzama tikai viena plata josla ar maksimumu 3,5 eV. Iegūto rezultātu kopums ļauj secināt, ka 1243 K temperatūrā 168 stundas atdedzinātās lodītes ar diametru 450 līdz 560 µm un vidējo grauda lielumu 10 µm ir radiācijas izturīgākas salīdzinājumā ar divu pārējo tipu lodītēm.

Артурс Зариньш, Арнис Супе, Гунта Кизане, Регина Книттер, Ингарс Рейнхолдс, Аигарс Витиньш, Вия Тилика, Андрис Ацтиньш. Радиолиз нестехиометрических шариков ортосиликата лития

Одна из технологических проблем реакторов ядерного синтеза - изменение состава и структуры литиевых материалов (Li_4SiO_4 или Li_2TiO_3) во время длительного воспроизведения трития . Цель работы - исследовать изменения состава и структуры керамических шариков Li_4SiO_4 при взаимодействии потока быстрых электронов (E = 5 МэВ, мощность дозы до 88 МГр•ч$^{-1}$, поглощенная доза до 10,6 ГГр) при температуре 543-573 K.

Нестехиометрические (2,5 % весовой части остатка SiO_2) шарики ортосиликата лития изготовлены в плавильно-распылительном процессе (Schott AG, Майнц, Германия). Исследованы три типа шариков с различным временем отжига, различным диаметром и размером зерна: отжиг 1 ч при 1073 K (диаметр <50 µм; размер зерна 1 µм), отжиг 128 ч при 1173 K (диаметр <50 µм, размер зерна 8 µм), отжиг 168 ч при 1243 K (диаметр 500 µм, размер зерна 10 µм). Продукты радиолиза исследованы применяя спектроскопию Фурйе и метод рентгено-структурного анализа. Термостимулированная люминисценция (ТСЛ) и спектроскопия парамагнитных центров (ПМЦ) использовалась для обнаружения радиационных дефектов.

Используя спектроскопию Фурйе и метод рентгено-структурного анализа констатированно образование новых фаз в облученных до 10,6 ГГр литиевых шариках. Идентифицировано присутствие LiOH, Li_2CO_3, Li_2SiO_3 и $Li_6Si_2O_7$. В спектрах ПМЦ всех трех образцов найдены линии SiO_4^{3-} (HC_2) и SiO_3^{3-} (E') радикалиона. но F^+ центры присутствуют только в спектрах ПМЦ шариков отожженных 1 ч при 1073 К. В кривых ТСЛ наблюдаются четыре максимума для всех трех типов шариков, но в оптических спектрах - только одна широкая полоса с максимумом при 3,5 эВ. Совокупность полученных результатов позволяет сделать заключение, что литевые шарики (диаметр от 450 до 560 мкм, средний размер зерна 10 мкм) отоженные 168 часов при температуре 1243 К более радиационно стойкие по сравнению с остальными двумя видами шариков.