Journal of Nuclear Materials 386–388 (2009) 286–289

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Study of Li_2TiO_3 + 5 mol% TiO_2 lithium ceramics after long-term neutron irradiation

Y. Chikhray [a,*], V. Shestakov [a], O. Maksimkin [b], L. Turubarova [b], I. Osipov [b], T. Kulsartov [c], A. Kuykabayeba [c], I. Tazhibayeva [c], H. Kawamura [d], K. Tsuchiya [d]

[a] Kazakh National University, Almaty, Kazakhstan
[b] Institute of Nuclear Physics, Almaty, Kazakhstan
[c] National Nuclear Center, Kurchatov, Kazakhstan
[d] JAEA, Oarai, Japan

ABSTRACT

Given work presents the results of complex material-science studies of 1 mm diameter ceramic pebbles manufactured of $Li_2TiO_3 + 5$ mol% TiO_2 ceramics before and after long-time neutron irradiation. Ceramic samples were placed in specially ampoules (six items) made of stainless steel Cr18Ni10Ti which were vacuumized and filled with helium. Irradiation of ampoules was carried out in the loop channel of WWRK reactor (Almaty, Kazakhstan) during 223 days at 6 MW power. After irradiation light-colored pebbles became grey-colored due to structure changes which generation of grey-colored inclusions (lithium oxide) with low density and microhardness. There is a radiation softening of lithium ceramic and that effect is higher for lower irradiation temperature 760 K than for 920 K. The value of maximum permissible load (pebble crash limit) at that is low and comprises ~37.9 N. The content of residual tritium is higher for ceramic irradiated at 760 K ($6.6 \pm 0.6 \times 10^{11}$ Bq/kg) than for ceramic irradiated at 920 K ($17 \pm 3 \times 10^{10}$ Bq/kg). The size change indicates that pebble increase more after irradiation at 760 K than at 920 K where the bigger portion of tritium leaves the pebble. X-ray analysis shows radiation modification of $Li_2TiO_3 + 5$ mol% TiO_2 phase composition and generation of new phases: $LiTi_2O_4$, $LiTiO_2$ and $Li_4Ti_5O_{12}$.

1. Introduction

Currently lithium containing ceramic materials such Li_2O, Li_2TiO_2, Li_2ZrO_3, Li_4SiO_4 etc. are considered as most promising candidates for tritium breeder in future fusion reactors. Some of these materials are well studied with respect to theirs behavior under irradiation but some are not. While taking into account that clause the goal of given paper was to gain new experimental results about the impact of long-term neutron irradiation and so generated tritium upon the structure and properties of lithium ceramic $Li_2TiO_3 + 5$ mol TiO_2. During this study the following tasks were solved: dismantling of experimental ampoules and safe storage of irradiated ceramic, measurements of residual tritium, examination of radiation effects and tritium content on ceramic structure, physical–mechanical properties and swelling of lithium ceramics, study of chemical composition.

2. Experimental procedure

The studied ceramic was of $Li_2TiO_3 + 5$ mol% TiO_2 composition. The samples shaped as balls (pebbles) with 1mm average diameter 2000 pcs in a number were placed in specially designed ampoules (6 pcs) made of Cr18Ni10Ti stainless steel, vacuumized and filled with pure helium. Irradiation was carried out in loop facility of Kazakhstan water–water research reactor (WWRK) under permanent control during 223 days at 6 MW of reactor power (Fig. 1). During irradiation of lithium ceramic at temperatures from 760 to 1170 K some ampoules (of A type, active) were monitored with respect to tritium yield [1,2] which was permanently generated in nuclear reactions. Some ampoules (of P type, passive) were not monitored with respect to tritium yield.

Irradiated samples were extracted from ampoules in a hot cell. Both unirradiated (control samples) and irradiated samples were studied with various methods including visual analysis of shape changes, density control, phase-structural analysis, mechanical test, examination of chemical composition changes with ICPMS and residual tritium measurements. Whit all this going on we tried to examine the same sample with all methods. All the time between examinations the samples were stored in vacuumized retorts.

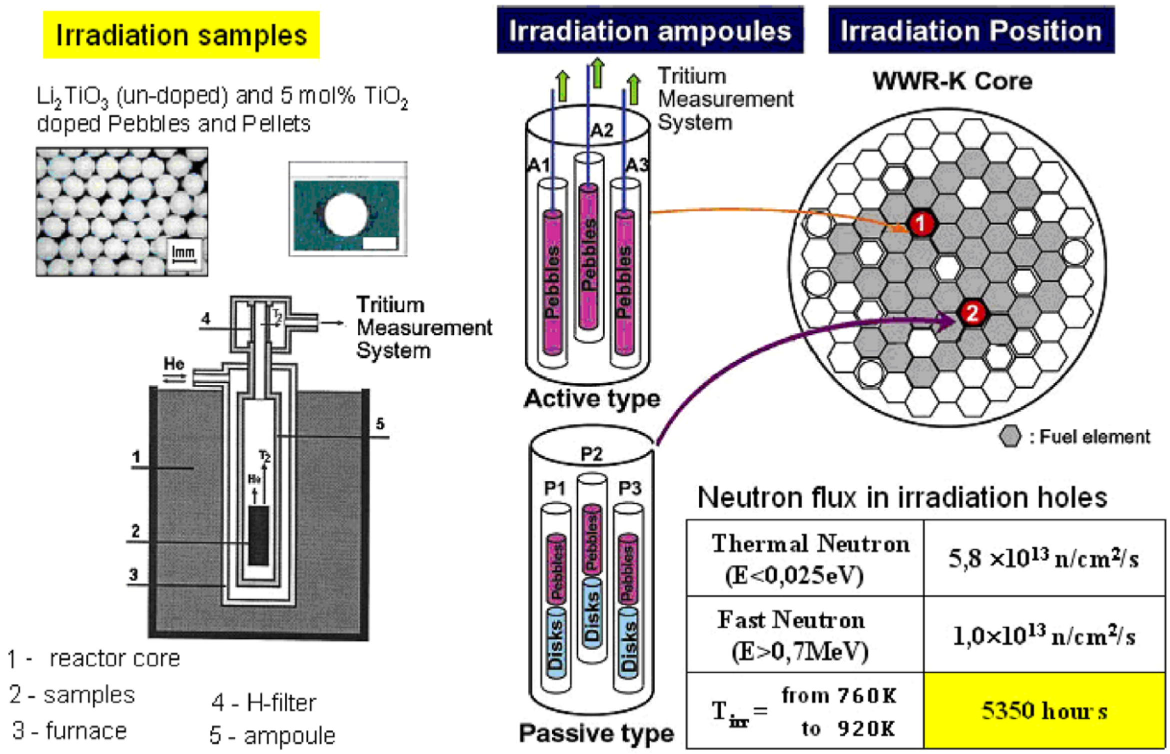
3. Results and discussion

Study of ceramic samples shape and size changes caused by reactor irradiation was carried out using digital thickness meter

---

* Corresponding author.
E-mail address: john@physics.kz (Y. Chikhray).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.12.111



Thermal Neutron (E<0,025eV)	5,8 ×10^{13} n/cm^2/s
Fast Neutron (E>0,7MeV)	1,0×10^{13} n/cm^2/s
T_{irr} = from 760K to 920K	5350 hours

Fig. 1. The schema of ceramic samples irradiation in WWRK reactor.

Sony (accuracy 1 micron) and instrumental microscope Karl Zeis with zoom 50. Based on results of thee different cross-section measurement the conclusion was made that they have not strict spherical form but a close to elliptical one.

Thereupon snapshots were took and used to derive average value of ellipse half-axes D_1 (short) and D_2 (long) and the ratio D_1/D_2 i.e. so called sphericity of a pebble. Also the average 'diameter' of pebble was derived too.

Analysis of size distributions curves shows that after irradiation at 760 K the most possible average pebble size is somewhat more than after irradiation at 920 K. Possibly it is related to that fact that at the same tritium generation rate its yield from pebble at 920 K is higher than at 760 K and that is the reason for smaller granular size.

It appears also that reactor irradiation changes the pebble color and they become grey totally or partially (Fig. 2).

The structure of ceramic pebbles was observed with optical microscope Neophot-2 with 1500 zoom. For that we've used the 'dry' mechanical grinding and polishing for production of petrographic thin sections. Examination of unetched sections of lithium ceramic pebbles disclosed three structural components of different colors: grey and dark inclusions are clearly apparent at light background. Light component prevail in initial unirradiated ceramic while the dark and grey inclusions dominate after irradiation only (Fig. 3).

X-ray structural analysis was used with purpose to identify grey and dark components in Li_2TiO_3 ceramic of irradiated and unirradiated samples. Phase-composition changes was registered with diffractometer system D8 ADVANCE (Bruker AXS GmbH) with CuKα-wavelength and position-sensitive flow-type transducer PSD-50 M.

As the result of X-ray diffractograms the following conclusion could be done: unirradiated Li_2TiO_3 ceramic pebbles are of single-phase Li_2TiO_3 ceramic with body-centered crystalline lattice. After irradiation at 920 K the pebbles from A3 ampoule disclose several phases at once: beside Li_2TiO_3 phase the main phase $LiTi_2O_4$ is clearly noted as well as the traces of face-centered cubic phase $LiTiO_2$.

Chemical composition changes in Li_2TiO_3 + 5 mol% TiO_2 ceramic were investigated using ELAN 9000 mass-analyzer with induction-coupled plasma. Using this instrument $^6Li/^7Li$ isotopic ratio was recorded.

The analysis result of lithium ceramic and calculated values of ^6Li burn-up are presented in Table 1.

Table 1 distinctly shows that ceramic pebbles irradiated at lower temperature (760 K) have a lower Li^6 isotope burn-up.

Fig. 2. Ceramic pebbles before (a) and after (b) irradiation.

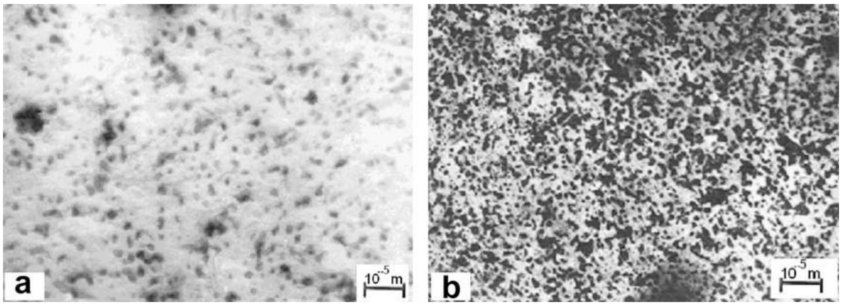


Fig. 3. Pebble's microstructure: (a) initial (unirradiated), light component prevail and (b) neutron irradiated at 920 K, lot of grey and dark inclusions.

Table 1
Content of lithium isotopes in Li_2TiO_3 + 5 mol% TiO_2 ceramic before and after irradiation.

Parameter	Before irradiation	After irradiation	
		T_{irr} = 760 K	T_{irr} = 920 K
Li^6 (mas.%)	95.4	94.3	94.0
Li^7(mas.%)	4.6	5.7	6.0
$^6Li/^7Li$	20.7	16.6	15.7
Li^6 burn-up (mas.%)	–	19.6	24.5

To investigate the reactor irradiation effect on ceramic strength parameters the unirradiated and irradiated pebbles were examined with mechanical compression test at temperature 293 K and deformation rate 0.5 mm/min. For that purpose a special tool (micro-chisel) was elaborated where universal test machine Instron-1195 was used as a loading unit.

Fig. 4(a) presents engineering diagrams obtained in deformation test of unirradiated pebbles (second curve is shifted along the *x*-axis for better view). The values of mechanical characteristics of ceramic pebbles derived from that diagrams are shown in Table 2 and are well agreed with results presented in [3–4] for unirradiated pebbles. So obtained data allows concluding that after irradiation at 920 K lithium ceramic become more brittle. In that time the effect of radiation softening appears more obviously in pebbles irradiated at 760 K (see Table 2).

In view of structure nonuniformity there is a clear interest to determine the strength of all ceramic's structural components. For that purpose we have used the results of microhardness measurements which were done with PMT-3 instrument.

It was stated that in irradiated pebble the 'dark' structure component is most fragile: H_μ = 85–95 kg/mm^2 (before irradiation ~130 kg/mm^2), while the 'light' component is the most solid: H_μ = 130–150 kg/mm^2 (before irradiation ~180 kg/mm^2).

Hence the results of microhardness measurements confirm the data on mechanical stress test and one can conclude that reactor irradiation leads to lithium ceramic softening. One of possible reasons for that is the presence of residual tritium in ceramic.

Measurements of residual tritium amounts in irradiated ceramic were carried out using the method of liquid scintillation with beta-spectrometer TRICARB-3100TR. As the result of all

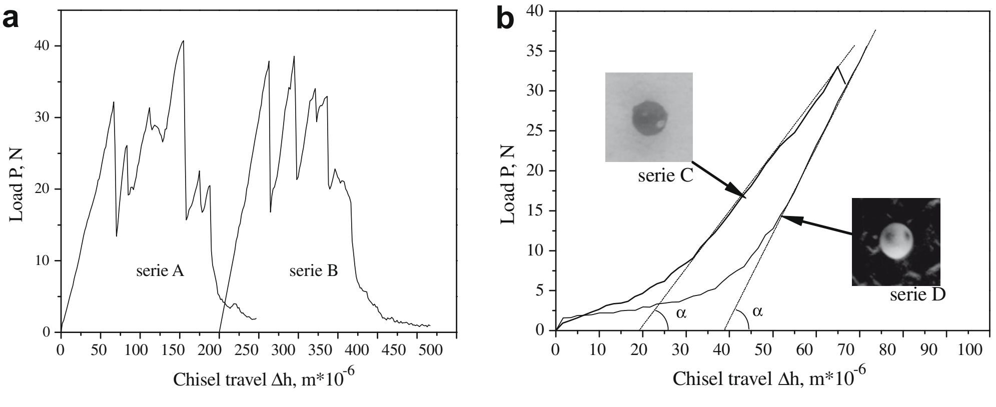


Fig. 4. Pebble stress diagrams: (a) unirradiated and (b) neutron irradiated (T_{irr} = 920 K).

Table 2
Strength characteristics of Li_2TiO_3 + 5 mol% TiO_2 ceramic before and after reactor irradiation.

Pebbles (series)	State	D_1, mm	D_2, mm	F_{avr}[a], mm^2	P_d[b], N	σ_d[c], MPa
A	Unirradiated	0.97	1.01	0.77	37.9	49.0
B		0.97	1.05	0.80	32.3	40.0
C (dark)	Irradiated (ampoule A3, *T* = 920 K)	1.07	1.00	0.84	32.5	38.7
D (light)		1.05	0.96	0.79	35	44.3
M8	T_{irr} = 760 K	1.053		0.8	15.8	18.2

[a] $F_{avr} = \pi D_{avr}^2/4$.
[b] P_d is maximal load at diagram.
[c] $\sigma_d = P_d/F_{avr}$.

examinations it was found that activity or residual tritium which was generated in ceramic under neutron irradiation at 920 K (average value of three measurements) comprise (17 ± 3) × 10^{10} Bq/kg. At the same time the activity of residual tritium from Li_2TiO_3 + 5 mol% TiO_2, pebble segment irradiated at 760 K appears higher and equal 6.6 × 10^{11} Bq/kg.

4. Summary

The results of preliminary complex material study of Li_2TiO_3 + 5 mol% TiO_2 lithium ceramic before and after long-term (5350 h) neutron irradiation at WWRK reactor at 760 K and 920 K disclose significant effect of radiation–thermal impact on ceramic pebbles structure and properties.

It is shown that after irradiation light-colored pebbles became grey-colored due to structure changes which generation of grey-colored inclusions with low microhardness. Based on ceramic's chemical composition study the conclusion was made that observer 'dark' inclusions in irradiated ceramic are lithium oxide while the 'light' component corresponds to titanium oxide.

It was found that there is a radiation softening of lithium ceramic and that that effect is higher for lower irradiation temperature 760 K than for 920 K. The value of maximum permissible load (pebble crash limit) at that is low and comprises ~37.9 N. At that the ceramic where 'light' component prevail is more solid than ceramic with 'dark' structure. Most possible reason for that is residual tritium ^3H which amounts are higher in pebbles irradiated at 760 K than in pebbles irradiated at 920 K.

From other hand the content of residual tritium is higher for ceramic irradiated at 760 K (6.6 ± 0.6 × 10^{11} Bq/kg) than for ceramic irradiated at 920 K (17 ± 3 × 10^{10} Bq/kg). Generally these data are in good agreement with the measurement results of pebble size change. The size change indicates that pebble increase more after irradiation at 760 K than at 920 K where the bigger portion of tritium leaves the pebble.

X-ray structure analysis shows radiation modification of phase composition of Li_2TiO_3 + 5 mol% TiO_2 ceramic and generation of new phases: $LiTi_2O_4$, $LiTiO_2$ and $Li_4Ti_5O_{12}$.

References

[1] V. Shestakov, I. Tazhibayeva, H. Kawamura, Y. Kenzhin, T. Kulsartov, Y. Chikhray, A. Kolbaenkov, F. Arinkin, Sh. Gizatulin, P. Chakrov, Fusion Sci. Technol. 47 (2005) 1084 (May).
[2] Y. Chikhray, V. Shestakov, T. Kulsartov, I. Tazhibayeva, H. Kawamura, A. Kuykabaeva, J. Nucl. Mater. Part 2 367–370 (1) (2007) 1028 (August).
[3] Kunihiko Tsuchiya, Hiroshi Kawamura. Data Base for Tritium Solid Breeding Materials (Li_2O, Li_2TiO_3, Li_2ZrO_3 and Li_4SiO_4) of Fusion Reactor Blankets, <http://www.hrc.toyama-u.ac.jp/f-blanket-database/f-index.html>.
[4] Kunihiko Tsuchiya, Hiroshi Kawamura, J. Nucl. Mater. 283–287 (2000) 1380.