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トリチウム増殖材データベース　(4)
(Li_2O, Li_2TiO_3, Li_2ZrO_3 and Li_4SiO_4 固体増殖材)

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Tritium Breeding Materials Data Base for Fusion Reactor Blankets (4)
(Li_2O, Li_2TiO_3, Li_2ZrO_3 and Li_4SiO_4 Solid Breeding Materials)

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ABSTRACT

This up-to-date compilation of data for ceramic breeding materials (Li_2O, Li_2TiO_3, Li_2ZrO_3, and Li_4SiO_4) is part of a study to construct a database for tritium breeding materials of fusion reactor blankets in which existing data for breeding materials and neutron multipliers have been collected from as many

sources as possible.

The data compiled include data on physical and thermal properties, mechanical properties, chemical stability and compatibility, tritium solubility and transport, irradiation effects, afterheat characteristics, thermal cycling effects, waste disposal, and other miscellaneous properties of ceramic breeding materials, such as Li_2O, Li_2TiO_3, Li_2ZrO_3, and Li_4SiO_4 . As a result of this compilation, the status of existing data can be recognized.

1. Introduction

Lithium containing ceramics, such as Li_2O, Li_2TiO_3, Li_2ZrO_3, and Li_4SiO_4, are recently considered as promising candidate tritium breeding materials for fusion reactor blankets. Up to this time, authors have endeavored to collect and compile data on many kinds of properties for those materials from as many literature as possible in order to construct a data base for them.

Then, authors rearrange data which have been collected until now, in order to recognize the status of collected data on a variety of properties for candidate breeder ceramics, and to plan the further investigation program for completing the construction of a database.

This compilation of data has made it clear in what properties of some materials there are uncertainties, discrepancies and good agreements. Therefore, it can be recognized what properties for candidate ceramics need more investigation.

This up-to-date compilation is a summary containing the our previous reports and newly collected data after the latest report.[3)]

2. Required characteristics for a solid breeding material

The functions of a solid breeding material are: 1) production of tritium from the neutron/lithium reaction and release of the tritium to purge stream; 2) production of thermal energy and conduction to the blanket coolant; and 3) shielding of neutrons. Thus, in evaluating breeding materials, the tritium retention/release properties are considered as primary parameters and the highest of the three. Particularly, solid breeding materials must efficiently perform these functions under high level of neutron exposure and high temperature conditions with maintaining their integrity during operation. Therefore, main required functions and characteristics for solid breeding materials are listed in Table 2-1. For the purpose of helping the evaluation of breeding materials, examples of breeding materials and operating conditions for a fusion reactor blanket are shown in Table 2-2.

Table 2-1 Main required functions and characteristics for solid breeding materials

Function	Required characteristics
Good tritium production, and Breeding characteristics	High lithium content Efficient release/recovery of produced tritium
Proper breeder temperature Control	High thermal conductivity
Good integrity	Good neutron irradiation resistance High mechanical strength, and high durability Good chemical stability Good compatibility with other materials
High safety	Low activation Low reactive with coolant
Fabrication	Mass production at a low price Easy treatment

Table 2-2 Major operating conditions of breeding materials of a fusion reactor.

	ITER	SSTR
Breeding material	Li_2ZrO_3	Li_2O
Li burn-up (%)	~5	10~30
Nuclear heat generation (MW/m^3)	~50	~90
Temperature range (°C)	300~750	450~950
Structural material	SS316 LV-IG	RAF(F82H)
Multiplier material	Be	Be
Environmental gas	He gas (~0.1MPa)	He gas (~0.1MPa)

ITER: International Thermonuclear Experimental Reactor.

SSTR: Steady State Tokamak Reactor.

3. Data for solid breeder materials

Up-to-date available data for the solid breeder materials are summarized in Table A-1, A-2, A-3, A-4. These tables are organized by material property in terms of physical properties, thermal properties, mechanical properties, chemical stability/compatibility/interaction with blanket coolant, purge gas, neutron multiplier and structural materials, tritium solubility/transport, irradiation effects, thermal cycle effects, and so on.

Representative properties of candidate breeder ceramics under the specified theoretical density (TD), porosity, and temperature, are summarized in Table 3-1. With numerical values of properties in Table 3-1, the evaluation on which candidate ceramic is considered to be superior to another ceramics, can be easily performed.

Moreover, the present status of breeder material database is shown in Table 3-2, in order to recognize the extent and degree of investigated data on properties for breeder materials.

4. Review of database on properties for candidate breeder ceramics

With regard to a variety of properties of breeder ceramics, the present status of an existing database for candidate breeder ceramics, such as Li_2O, Li_2TiO_3, Li_2ZrO_3, and Li_4SiO_4, was shown in Table 3-2.

4.1 Physical and thermal properties

In tritium breeding ratio (TBR), Li_2O is considered the only ceramic candidate among Li_2TiO_3, Li_2ZrO_3, and Li_4SiO_4 for achieving a TBR larger than unity in the absence of a neutron multiplier.

As for the vapor pressure data, more investigation is required in order to develop a reliable database for breeder ceramics.

4.2 Mechanical properties

The thermal cycling behavior of pebbles 1 mm in size was investigated for Li_2O (92%TD, 42 μm grain size), Li_2ZrO_3 (80%TD, 40 μm grain size), and Li_4SiO_4(93%TD, 40 μm grain size) under the representative conditions in ITER, i.e. 400-800°C and the heating-cooling rates of 20°C/s(72,000K/h) up to 2000 cycles.[68] While the Li_2O pebbles performed extremely well, the Li_2ZrO_3 and Li_4SiO_4 pebbles fractured significantly. In contrast, Li_4SiO_4 pebbles 0.4-0.6 mm in size cycled for 50 cycles, showed good behavior. Moreover the thermal cycling behavior of pebbles 1.2 mm in size for Li_2TiO_3 was investigated under 273-1273K at 200 K/h ramp temperature change. The results were summarized in Table 4-1.[63]

Table 4-1 Effects of thermal cycling on strength of Li_2TiO_3 pebbles

Sample	Strength	Number of thermal cycles					
		0	3	6	9	12	15
77.6% TD 4~10 μm grain	Compressive Strength (N)	40.9	44.9	43.1	42.7	42.3	42.7
81.3% TD 40~140μm grain	Compressive Strength (N)	35.6	4.4	9.8	33.4	32.5	31.1

The thermal cycling behavior of Li_2ZrO_3 pellets (76.8%TD and 83.5%TD, 8mm length), cycled in the temperature range of 330~550°C, performed well. No fracture was observed after 1000 cycles at an equivalent tangential tensile stress of 30 MPa; 14% fracture was observed for the pellets with 76.8%TD after 10000 additional cycles at 40 MPa. No fracture was observed for the pellets with 83.5% TD Li_2ZrO_3 after 30000 cycles at 47 MPa. The higher the density is, the better is the behavior. Li_2TiO_3 pellets thermal cycling test is in progress. From the first results, Li_2TiO_3 pellets behavior is expected to be similar to that of Li_2ZrO_3 pellets .For the effects of thermal cycling behavior of Li_2TiO_3, Li_2ZrO_3, and Li_4SiO_4 more data are needed.

4.3 Chemical stability and compatibility (Interaction with other blanket materials)

In laboratory tests, the interaction of beryllium with Li_2ZrO_3 and Li_4SiO_4 was found to be negligible up to 650°C.[68] Interaction of Li_2TiO_3 with steels is less than that of Li_2ZrO_3.

The irradiation effect on the interaction of beryllium and lithium ceramics was investigated. No irradiation effect was detected under the conditions explored at ^6Li burn-up of 20%-40% for natural ^6Li isotope content (Li burn-up of 1.5%-3%).[68]

Lithium contained in Li_2ZrO_3 sintered compacts immersed in water, is slowly but completely dissolved within one month, whereas no dissolution of lithium contained in Li_2TiO_3 sintered compacts is detectable after a 40 days immersion. Also, no uptake of moisture from room air after 6 months exposure is reported on Li_2TiO_3. Both ceramics are easily soluble in hydrochloric acid.

The tritium solubility data for Li_2O/H_2O are quite good, but the solubility data for Li_2O/H_2 system are quite scattered (factor of 15 spread in the data). The desorption/decomposition data for moisture release from LiOH and Li_2O have a factor of 10 scatter. Adsorption for Li_2O/H_2 and Li_2O/H_2O system needs to be more reasonably characterized. Solubility/adsorption/desorption mechanisms are only poorly characterized for Li_2ZrO_3, Li_4SiO_4 and Li_2TiO_3 ceramics.

4.4 Irradiation effects

(1) Irradiation behavior

Under conditions of temperature levels of 500, 700, 900°C and up to 3% lithium burn-up, Li_2ZrO_3 showed that swelling was low, physical integrity was excellent, no change of grain size was observed, and tritium and helium retention was very low. On the contrary, Li_2O did high swelling at 3 % burn-up.

After irradiation to 3% burn-up, there was a significant reduction in the thermal conductivity of Li_2O at low temperatures, i.e. under 400°C. At higher temperatures, thermal conductivity values were unchanged or were even higher than the unirradiated values.[68]

No testing of irradiation behavior of Li_2TiO_3 ceramic was almost made to date, except for a few tests of tritium and helium retention, and tritium release. However, the authors suppose that the behavior will be similar to that of Li_2ZrO_3 from our view of reference materials.

(2) Tritium release

For safety and economical reasons the tritium release rate must be enough large that the tritium inventory in the blanket does not become excessive. Tritium residence time (τ) defined as the average time a triton spends in the breeder between generation and release, can be used to relate the tritium inventory to the tritium generation rate.

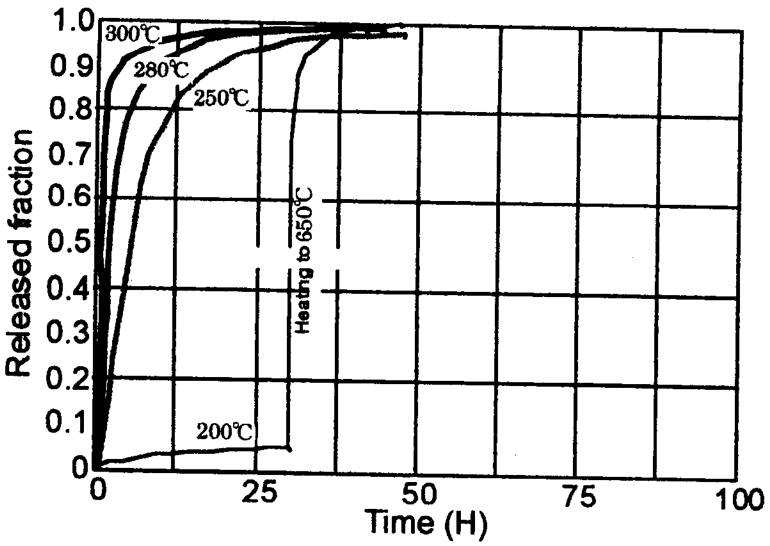

Fig. 4-1 Isothermal tritium release at 300°C, 280 °C, 250°C, 200°C, in He + 0.1%H_2 purge gas, flow rate 2.4 l/h for Li_2TiO_3

Tritium residence times were investigated for Li_2O. Li_2ZrO_3[6], and Li_4SiO_4[68] at various temperatures.

The effects of lithium burn-up on tritium release for Li_2ZrO_3 was studied at 4.5%, 7.6% and 9.5% lithium burn-up. Those results reveal no decrease in the tritium release. For the comparison of the tritium release behavior of Li_2ZrO_3 and Li_2TiO_3 up to 9.5% lithium burn-up, examples of test results are shown in Figs.4-1 and 4-2. These results indicate that those behave similarly. For Li_2ZrO_3 a good tritium release is observed down to 200°C, i.e., 40% tritium released within about 120h. For Li_2TiO_3 a larger decrease in the tritium release between 250°C and 200°C is observed. This difference in behavior with Li_2ZrO_3 reflects the difference in the shape of the tritium release peaks in the linear heating run i.e., sharper peak for Li_2TiO_3 than for Li_2ZrO_3.

As the estimated minimum temperature for which the residence time is one day, is desirable to be lower from a design viewpoint, the tritium release performance of Li_2ZrO_3 and Li_2TiO_3 are superior to Li_2O and Li_4SiO_4. Because Li_2O and Li_4SiO_4 are not

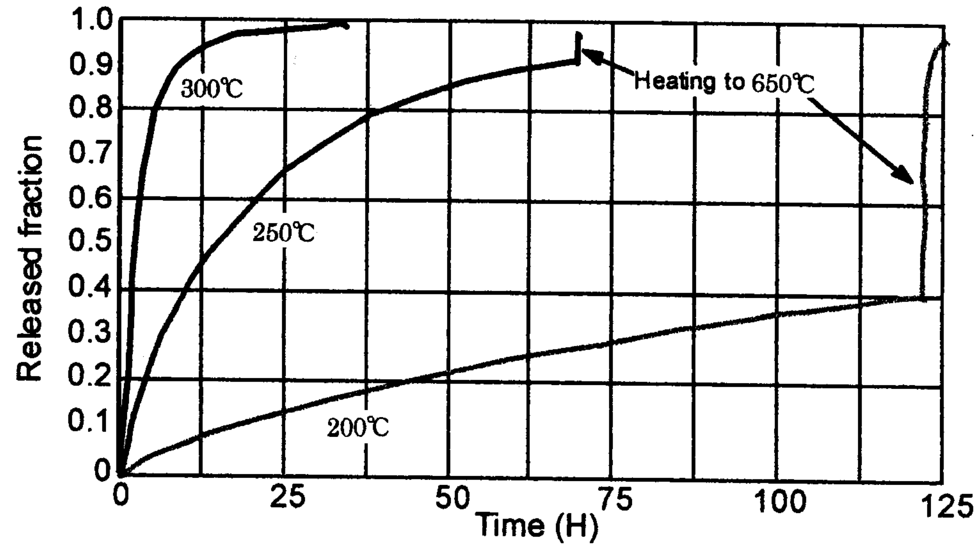

Fig. 4-2 Isothermal tritium release at 300°C, 250°C, 200°C, in He + 0.1%H_2 purge gas, flow rate 2.4 l/h for Li_2ZrO_3

releasing tritium at low enough temperature and/or are too reactive with water.

Therefore, more data are needed for tritium retention and release of Li_2TiO_3, and more data for helium retention and release are also needed.

(3) Waste disposal

With respect to waste disposal, one must consider the production of long-life radionuclides. For the ceramics, the radioactivity after 1 year is very low in comparison with that of the structural materials. In all cases, activation of the structural materials is higher than that of ceramic breeding materials. The long-life radionuclides, such as $^{94}Nb(L_{1/2}=2x10^4y)$, are decay products from Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3. Li_2O does not present a problem for waste disposal. With no impurities, the U.S. Class C waste disposal rating for Li_2TiO_3 is roughly equal to that for Li_2O and Li_4SiO_4 and more than 10 times lower than Li_2ZrO_3.

Afterheat levels in Li_2TiO_3 are 20~50 times more than in Li_2O and Li_4SiO_4, but 2~100 times lower than Li_2ZrO_3.

5. Concluding Remarks

Authors have compiled the up-to-date data for candidate blanket solid breeding materials which have been collected by this time, and somewhat assessed these data. There are less data for Li_2TiO_3 than those for Li_2O, Li_2ZrO_3 and Li_4SiO_4, since Li_2TiO_3 is recently considered as an attractive candidate breeding material.

As a whole, physical properties and thermal properties are fairly good investigated, but the investigations are not enough. More investigations on fracture strength, specially, tensile strength for breeder ceramics, are required. Data on thermal creep for Li_2TiO_3 are required.

With regard to compatibility, the data on hydrogen solubility and adsorption for Li_2ZrO_3, Li_4SiO_4 and Li_2TiO_3 are needed. Also the data on water vapor solubility and adsorption for Li_2ZrO_3, Li_4SiO_4 and Li_2TiO_3 are needed.

For lack of enough data on irradiation effects for breeder ceramics, it is hereafter more needed to investigate irradiation behaviors on physical properties, thermal properties, mechanical properties, tritium transport, retention and release properties, helium transport, retention and release properties, fracture properties, and so on. In this case, Table 3-2 will be helpful for investigators. The more information on tritium release and thermal cycling behavior for Li_2TiO_3 is needed.

However, owing to the limitation of our research and search activity, there may be still oversight of existing data. So the authors are very much grateful for being notified existing data as well as being assisted for collecting the data and/or supplied with them. Only with such collaboration, we can construct the complete database on breeding blanket materials.

Acknowledgement: The authors wish to thank Professor and Dr. K. Watanabe for his continuos and helpful advice.

Table 3-1 Summary of candidate ceramic breeder characteristics.

Property	Li_2O	β Li_2TiO_3	Li_2ZrO_3	α Li_4SiO_4
Density, 100%TD, g/cm^3	2.03	3.43	4.16	2.40
Lithium density, g/cm^3	0.94	0.43	0.38	0.55
Phase change temp. °C Melting point. °C	370 1432 ± 6	1150 1535	1100 1695 ± 15	660 1255
Thermal conductivity W/m.K, 500°C,@ 85%TD Unirradiated	4.4	1.8	1.9	0.9
Thermal expansion, @ RT-700°C, % 600°C 1/K	1.9 26x10^{-6}	1.2 21 x10^{-6}	0.7 9.96 x10^{-6}	1.8 24 x10^{-6}
Thermal diffusivity At 600°C, mm^2/s	0.85	0.55	0.357	0.300
Young's modulus, GPa RT,& 600°C	70.0 & 60.7	123(300K, 80%TD,1~2 μ m)	89.0& 77.3	56.3& 48.2
Poisson's ratio, RT,& 600°C	0.19 & 0.19	0.24(300K, 80%TD)	0.2 & 0.2	0.24 & 0.24
Bending strength, MPa @RT,85%TD,10 μ m grains	60	60	60	50
Compressive strength, MPa, RT & 600°C	(65.8)&(28.4)	--	145 &(---)	253 &(--)
Temperature for 0.1 Pa Li Vapor pressure, °C	1120	~ 1300	1300	1210
1- D TRR (optimum % ^{6}Li)	1.46(20)	1.32(51)	1.38(58)	1.34(33)
Creep rate, μ m/m-s (800 °C, 20 MPa)	4.0	--	(≪2)	0.184
Swelling, vol,% @ 700°C,2 at%Li burnup	7.5	--	0.5	1.2
Tritium residence time, hr @ 400°C, 80%TD, 1 μ m grains	1	< 1	< 1	14
Class C waste disposal Rating, @ 15MW.yr/m^2, 10 yr cooling	0.2	0.17	24	0.14
Afterheat, W/cm^3 @ 1hr, 15 MW.yr/m^2, 85%TD	0.001* 10^{-9} **	0.05 *	6 * 0.05 **	0.003 * 0.0001 **
Steel reaction layer, μ m @ 500°C, 10^4 hr, 10 Pa H_2O	8 - 50	< 7	7	20
Be reaction layer, μ m @ 700°C, 10^4 hr, 10 Pa H_2O	~200	--	~50 – 100	200 – 600

Note: 1. Properties of Young's modulus, Poisson's ratio, compressive strength and creep rate, at 80 % TD, 10 μ m grain diameter and 90 % Li-6 enrichment.

2. Values in parentheses are estimated or extrapolated well beyond the data base.

3. * From FINESSE 1987(p.2-125); no impurities; tritium retained in breeder.

4. ** From UKAEA 1989; 12.5 MW.yr/m^2, no impurities or tritium.

Table 3-2 Data Base Assessment for Solid Breeders (Breeder Ceramics)

	Li_2o	Li_2TiO_3	Li_2ZrO_3	Li_4SiO_4
Physical and thermal properties				
Density	■	■	■	■
Melting point	■	■	●	▲
Vapor pressure	▲	○	○	○
Thermal expansion	■	▲	▲	▲
Thermal conductivity	▲	▲	▲	
Specific heat	■	▲	▲	■
Mechanical properties				
Young's modulus	▲	▲	▲	▲
Poisson's ratio	▲	▲	○	▲
Fracture strength				
tensile				
compressive	○	○	○	○
bending	○	○	▲	▲
Creep properties	▲		○	▲
Chemical stability/compatibility				
Composition/purity	■	■	■	■
Stability	■	■	■	■
Vapor pressure/transport	■	○	○	○
Compatibility				
water	▲	■	■	▲
beryllium			▲	■
Stainless Steel	○	▲	▲	■
Tritium solubility/transport				
Tritium solubility	●			
Tritium diffusivity	■		○	○
Adsorption/desorption	●			
Radiation effects				
Physical properties	○		○	○
Swelling	○		○	○
Creep				
Tritium trapping/transport	●	○	○	○
Helium trapping/transport	○	○	○	○
Fracture properties	○	○	○	

Note: 1. ■ ---------Adequate data base and good agreement
2. ▲----------Limited data base and general agreement
3. ●----------Limited data base and important discrepancies (new data sets have become available)
4. ○----------Single set of limited is available.
(More investigations are required)
5. Blank---------Very limited/non-existent/high uncertainties
(More investigations are required)

Table A-1 Physical and thermal properties of candidate breeder materials

1. Li_2O

1.1 Physical properties

Item	Data	Refs.
Molecular weight, g/g-mol	$30.0314 - 2.002\,\delta$, δ = atom fraction ^{6}Li in Li	9
Crystalline structure	Cubic	9
Density, g/cm^3	$2.0338\,(1 - 0.06665\,\delta)$	10
Li density, g/cm^3	$0.815\,\delta$ for ^{6}Li, $0.950(1-\delta)$ for ^{7}Li,	10
Melting point, °C	1432 ± 6	9

1.2 Thermal properties

Item	Data	Refs.
Vapor pressure, Pa	$\log P(Li) = -(18.19 \times 10^3/T) + 12.09$ $\log P(LiO) = -(19.85 \times 10^3/T) + 11.21$ $\log P(Li_2O) = -(20.60 \times 10^3/T) + 13.40$ $1532 \leqq T \leqq 1073$ K	11
Specific heat, kJ / kg-K	$Cp = 2.5179 + 3.328 \times 10^{-4}T - 8.382 \times 10^4/T^2$ $306 \leqq T \leqq 1073$ K	10
Thermal conductivity, W/m-K	$\kappa = (1-p)^{1.96}\ [39.79\,(1 + 7.067 \times 10^{-3}T)^{-1}]$ $0.066 \leqq$ p(porosity) $\leqq 0.292$, $473 \leqq T \leqq 1173$ K	12
Thermal expansion Linear expansion, %. Instantaneous coef. 1/K Mean coef. 1/K	 $\Delta L/L_0 = 1.87 \times 10^{-3}(1 + 4.49 \times 10^{-4}T)(T - 298)$ $\alpha = 1.605 \times 10^{-5}(1 + 1.072 \times 10^{-3}T)$ $\alpha_m = 1.87 \times 10^{-5}(1 + 4.49 \times 10^{-4}T)$ $298 \leqq T \leqq 1223$ K	10

2. $\beta\,Li_2TiO_3$

2.1 Physical properties

Item	Data	Refs.
Molecular weight, g/g-mol.	$109.93\,(1 - 1.82 \times 10^{-2}\,\delta)$, δ = ^{6}Li fraction in Li	9
Crystalline structure	Monoclinic	9
Density, g / cm^3	$3.44\,(1 - 1.82 \times 10^{-2}\,\delta)$	9
Li density, g / cm^3	$0.37\,\delta$ for ^{6}Li, $0.44(1-\delta)$ for ^{7}Li,	9
Melting point, °C	1545	9

2.2 Thermal properties

Item	Data	Refs.
Vapor pressure	Temperature at which total lithium vapor pressure is 0.01Pa, K $839 + (305 + 87.3 \log 100P(D_2O)]\ ) - 78.3 \log P(D_2)/$ $[1+2.55 \times 10^{-10} \log 100P(D_2O)^{18.6}]$ $10 \leqq P(D_2) \leqq 1000$ Pa, $0.01 \leqq P(D_2O) \leqq 100$ Pa	13 14 15 16
Specific heat, kJ / kg-K	$355\,(T - 100)^{1.1}/(1+0.3\,T^{1.05})$ $300 \leqq T \leqq 1400$K	****
Thermal conductivity. W/m-K	$(1-\varepsilon)^{2.9}(5.35 - 4.78 \times 10^{-3}T + 2.87 \times 10^{-6}T^2)$ $0.14 \leqq \varepsilon$ (porosity) $\leqq 0.25$, $400 \leqq T \leqq 1400$ K	9, 21, 6, 20
Pebble bed thermal conductivity, W/m-K	$(1-\varepsilon)[0.74+0.00015\,(T-273)+3.3 \times 10^{-7}(T-273)^2]/0.52$ 0.7~1.2 mm diameter pebble, 0.1 MPa He $0.43\,14 \leqq \varepsilon$ (smear porosity) $\leqq 0.48$,	22

	$300 \leqq T \leqq 1300$ K	
Thermal expansion Linear expansion, % from 293 K Instantaneous coef. 1/K Mean coef. from 293K, 1/k	$\Delta L/L_0 = -0.4119 + 1.154 \times 10^{-3} T + 5.505 \times 10^{-7} T^2$ $\alpha = 1.154 \times 10^{-5} + 1.101 \times 10^{-8} T$ $\alpha_m = (-0.004119 + 1.154 \times 10^{-5} T + 5.505 \times 10^{-9} T^2)/(T - 293)$ $373 \leqq T \leqq 1073$ K	6

**** : 9, 17, 18, 19, 6, 20

3. Li_2ZrO_3

3.1 Physical properties

Item	Data	Refs.
Molecular weight, g/g-mol	$153.25(1 - 1.31 \times 10^{-2} \delta)$, δ = ^{6}Li fraction in Li	9
Crystalline structure	Monoclinic	9
Density, g/cm^3	$4.1573(1 - 1.31 \times 10^{-2} \delta)$	9
Li density, g/cm^3	0.3264δ for ^{6}Li, $0.3807(1-\delta)$ for ^{7}Li,	9
Melting point, °C	1695 ± 15	24,24

3.2 Thermal properties

Item	Data	Refs.
Vapor pressure, Pa	$\log P(Li) = -18.39 \times 10^3/T + 10.69$ $1031.. \leqq T \leqq 1642$ K	25
Specific heat, kJ/kg-K	$Cp = 1.022 - 3.696 \times 10^{-5} T - 2.791 \times 10^4 T^{-2}$ $350 \leqq T \leqq 1012$ K	26
Thermal conductivity, W/m-K	$k = (1-\varepsilon)^{5/3}[3.643(1+1.549 \times 10^{-3} T)^{-1} + 7.579 \times 10^{-10} T^3]$ $0.187 \leqq \varepsilon$ (porosity) $\leqq 0.211$, $373 \leqq T \leqq 1063$ K	27
Thermal expansion Linear expansion, % Instantaneous coef. 1/K Mean coef. 1/K	$\Delta L/L_0 = 9.89 \times 10^{-4}(1 + 1.13 \times 10^{-5} T)(T - 298)$ $\alpha = 9.86 \times 10^{-6}(1 + 2.27 \times 10^{-5} T)$ $\alpha_m = 9.89 \times 10^{-6}(1 + 1.13 \times 10^{-5} T)$	22

4. α Li_4SiO_4

4.1 Physical properties

Item	Data	Refs.
Molecular weight, g/g-mol	$120.126(1 - 3.315 \times 10^{-2} \delta)$, δ = ^{6}Li fraction in Li	9
Crystalline structure	Monoclinic	9
Density, g / cm^3	$2.3993(1 - 3.332 \times 10^{-2} \delta)$	10
Li density, g / cm^3	0.4805δ for ^{6}Li, $0.5604(1-\delta)$ for ^{7}Li,	10
Melting point, °C	1255	9

4.2 Thermal properties

Item	Data	Refs.
Vapor pressure, Pa	$\log P(Li) = 14.948 - 23602/T$ $\log P(O_2) = 14.769 - 24473/T$ $\log P(Li_2O) = 21.651 - 36223/T$ $1385 \leqq T \leqq 1516$ K $\log P(LiOH) = 8.686 - 11580/T$ at $P(H_2O) = 10.1$ Pa	29 30
Specific heat, kJ / kg-K	$Cp = 0.890 + 1.46 \times 10^{-3} T + 4.01 \times 10^3 T^2$ $272 \leqq T \leqq 873$ K	9,10 28

Thermal conductivity, W/m-K	$k = (1-\varepsilon)^{5/3}(2.49)[(1+2.06\times10^{-3}T)^{-1} + 1.85\times10^{-10}\ T^3]$ $0.16 \leqq \varepsilon$ (porosity) $\leqq 0.30$, $373 \leqq T \leqq 873$ K	31 32
Thermal expansion Linear expansion, % Instantaneous coef. 1/K Mean coef. 1/K	$\Delta L/L_0 = 1.267\times10^{-3}(1+1.065\times10^{-3}T)(T-298)$ $\alpha = 8.669\times10^{-6}(1+1.312\times10^{-3}T)$ $\alpha_m = 121.67\times10^{-6}(1+1.065\times10^{-3}T)$ $298 \leqq T \leqq 1273$ K	33

Table A-2 Mechanical properties of candidate breeder materials

1. Li_2O

Item	Data	Refs.
Young's modulus, GPa	$E = 141\exp(-3.5p)[1-2.3\times10^{-4}(T-293)]$ $0.07 \leqq p \leqq 0.20$, $T = 293$ K	34
Poisson's ratio	$\nu = 0.19$ (93% dense pellet), $T = 293$ K $= 0.16$ (single crystal), $298 \leqq T \leqq 1603$ K	35
Ultimate compressive strength, MPa	$\sigma_c = 800\, dg^{-0.5}\exp(-10p) \cdot (2000/T)$ dg = grain diameter in μm.	34
Ultimate bending strength, MPa	$\sigma_b = 195\, dg^{-0.5}\exp(-4.3p) \cdot (2000/T)$ dg = 10 μm, p = 0.2, T = 293 K	34
Tensile failure strength, MPa	$\sigma_{ft} = 195\, dg^{-0.5}\exp(-4.3p) \cdot (2000/T)$ dg = 10 μm, p = 0.2, T = 293 K	34
Thermal creep rate, 1/s	$\varepsilon_c = 8.8\times10^2(1-p^{2/3})^{-n}\exp(-4.04\times10^4/T)\,\sigma^n$ $n = 5.9$ for $T < 973$ K $n = 5.9[1-1.1\times10^{-3}(T-973)]$, $973 \leqq T \leqq 1123$ K $n = 4.9$ for $T > 1123$ K $0.07 \leqq p \leqq 0.21$, $973 \leqq T \leqq 1223$ K, $4 \leqq \sigma \leqq 45$ MPa	34

2. βLi_2TiO_3

Item	Data	Refs.
Young's modulus, GPa	$266.8(1-\varepsilon)(1-1.2\varepsilon)^2$ $0.1 \leqq \varepsilon$ (porosity) $\leqq 0.3$, 300 K, 1~2 μm grains	6
Poisson's ratio	$0.3(1-\varepsilon)$, $0.1 \leqq \varepsilon$ (porosity) $\leqq 0.3$, 300 K	6
Rupture strength, MPa	$170(1-2.27\varepsilon)$, $0.1 \leqq \varepsilon$ (porosity) $\leqq 0.3$, 300 K, 1~2 μm grains size	36
Bending strength, MPa	60, 300 K, 85 % T.D. 10 μm grains size	36
Pebble crush strength, N	30 Weibull (4~ 10 μm grains, 85 % dense, 1.2 mm) 40 Weibull (40~ 140 μm grains, 78 % dense, 1.2 mm) 40 Mean (~ 20 μm grains, 67 % dense, 1.6 mm)	22 37
Vickers hardness, MPa	$363(1-2.36\varepsilon)$, $0.1 \leqq \varepsilon \leqq 0.3$, 300 K,	6
Thermal creep rate, 1/s	No data	

3. Li_2ZrO_3

Item	Data	Refs.
Young's modulus, GPa	$E = 203.5(1-p)(1-1.286p)^2[1-2.40\times10^{-4}(T-293)]$ T = 293 K, p = porosity	38

Poisson's ratio	$\nu = 0.2$	39
Ultimate compressive strength, MPa	$\sigma_c = 396$, dg (grain diameter in μm) = 0.8 μm, 80 % T.D. $\sigma_c = 230 \pm 31$, dg = 2 μm, 80 % T.D.	38 26
Ultimate bending strength, MPa	$\sigma_b = 65 \pm 15$ (25 °C), 60 ± 20 (400 °C), 63 ± 1 (600 °C) dg = 2 μm, 80 % T.D.	26
Vickers hardness, MPa	$504.6 (1 - 2.36 \varepsilon)$, ε = porosity, 263.4 (80 % T.D.)	6
Thermal creep rate, 1/s	2×10^{-6} (26 MPa), 8×10^{-6} (745 MPa), 4×10^{-5} (144 MPa) at 900 °C	40

4. αLi_4SiO_4

Item	Data	Refs.
Young's modulus, GPa	$E = 110 (1 - p)^3 [1 - 2.5 \times 10^{-4} (T - 293)$ $0.02 \leqq p$ (porosity) $\leqq 0.32$, 293 K,	41 42
Poisson's ratio	$\nu = 0.24$, $p = 0.1$, $T = 293$ K	42
Ultimate compressive strength, MPa	$\sigma_c = 975 \, dg^{-0.44} (1 - p)^{1.5}$, $15 \leqq dg \leqq 100$ μm $0.06 \leqq p \leqq 0.28$, 293 K, (dg = grain diameter in μm.)	42
Ultimate bending strength, MPa	$\sigma_b = 275 \, dg^{-0.5} \exp(-4.3 p)$, $4 \leqq dg \leqq 50$ μm $0.02 \leqq p \leqq 0.32$, $T = 293$ K	41
Tensile failure strength, MPa	$\sigma_{ft} = 150 \, dg^{-0.5} \exp(-4.3 p) \cdot (1850 / T)$ $4 \leqq dg \leqq 50$ μm, $0.02 \leqq p \leqq 0.32$, $T = 293$ K	34
Thermal creep rate, 1/s	$\varepsilon_c = 1.4 \times 10^{-2} \exp(-2.5 \times 10^3 / T) \sigma$ $10 \leqq \sigma \leqq 40$ MPa, $0.08 \leqq p \leqq 0.22$, $1000 \leqq T \leqq 1220$ K	42

Table A−3 Chemical stability and compatibility (interaction with other materials)

1. Li_2O

Item	Data	Refs.
Hydrogen Solubility in Li_2O, (H) ppm (Li_2O)	$S_H = 7.1 \exp(-2000 / T) P(H_2)^{0.5}$ $20 \leqq P(H_2) \leqq 200$ Pa, $476 \leqq T \leqq 963$ K	43
Interaction with Water Liquid	$Li_2O + H_2O \rightarrow 2 LiOH + 125$ kJ / mole LiOH	9
Water Vapor Solubility. (OH) ppm (Li_2O)	$S_H = 10^{-A} [9.864 \times 10^{-6} P(H_2O)]^B$ $A = 23.667 - 2.502 \times 10^{-2} T + 9.62 \times 10^{-6} T^2$ $B = 0.427 + 1.7 \times 10^{-4} T$ $2 \leqq P(H_2O) \leqq 2000$ Pa, $713 \leqq T \leqq 1123$ K	44
Interaction with 316 S.S. (wastaage), mm	$d = 1.06 \times 10^3 \exp(-5920 / T) t^{0.5}$ $773 \leqq T \leqq 1073$ K, $100 \leqq t \leqq 5600$ h	45,46 47
Interaction with Be	No data	

2. βLi_2TiO_3

Item	Data	Refs.
Hydrogen Solubility,	$\leqq 3 \times 10^{-7} \exp(3600 / T)$ mol fr. / $Pa^{0.5}$ $73 \leqq T \leqq 773$ K, 2 ~ 100 Pa	22
Hydrogen Adsorption	No data	
Interaction with Water	Low solubility in water ≪ 1 % uptake after 6 month exposure to room air	6
Interaction with Be	No data	

Interaction with 316 S.S. penetration depth, μm	$3600\ t^{0.5} \exp(-9000/T)$ 0.1 MPa He, $823 \leqq T \leqq 923$ K, $410 \leqq t \leqq 1023$ h	21
Interaction with Acids, Li dissolution	90 % after 4 hrs in 95 % aqua-regia+5 % HF 84 % after 15 hrs in 1 M HNO_3 at 323 K	6,21 22,48

3. Li_2ZrO_3

Item	Data	Refs.
Hydrogen Solubility	No data	
Hydrogen Adsorption	No data	
Interaction with Water Liquid	Hydrolyses at 25 ℃ and 100 ℃	26,44 38
Water Vapor Solubility	No data	
Water Vapor Adsorption	No data	
Interaction with Steels	No significant interaction in conditions explored: up to 700 ℃ in vacuum	45
Interaction with Be	No significant interaction up to 650 ℃ in vacuum slight oxidation of beryllium in wet helium	50

4. α Li_4SiO_4

Item	Data	Refs.
Hydrogen Solubility, (H) ppm (Li_4SiO_4)	No data	
Interaction with Water Liquid	No data	
Water Vapor Solubility, (OH) ppm (Li_4SiO_4)	No data	
Water Vapor Adsorption, mols (OH) / m^3	No data	
Interaction with Steels, Dry, penetration depth, mm	$d^2 = 1 \times 10^5\ t \ \exp(-1.20 \times 10^4/T)$ $25 \leqq t \leqq 500$ h, $973 \leqq T \leqq 1273$ K	45
Interaction with Steels, P(H_2O) at 10 Pa penetration depth, mm	$d^2 = 2.5 \times 10^5\ t \ \exp(-1.20 \times 10^4/T)$ $25 \leqq t \leqq 500$ h, $973 \leqq T \leqq 1273$ K	51
Interaction with Be, penetration depth, mm	$d^2 = 1.1 \times 10^5\ t \ \exp(-1.02 \times 10^4/T)$ $100 \leqq t \leqq 1000$ h, $923 \leqq T \leqq 1023$ K	52

Table A-4 Irradiation effects and miscellaneous effects of candidate breeder materials

1. Li_2O

1.1 Irradiation effects

Item	Data	Refs.
Physical integrity	Fair for 500, 700, 900 ℃ (< 3 at. % ^6Li burn- up) Fair for 550 ~ 1000 ℃ (4 at. % ^6Li burn- up)	47 53
Swelling	$\Delta V / V_0$, % Burn- up at. % 500 ℃ 700 ℃ 900 ℃ 1 -1.0 5.0 6.0 2 -3.5 7.5 6.0 3 -2.8 7.0 6.0	47

Grain growth, μm at 1 at. % ^{6}Li burn-up	500 ℃ 700 ℃ 900 ℃ $3.5 \rightarrow 3.5$ $3.5 \rightarrow 7.0$ $3.5 \rightarrow 17.0$	54
Helium retention	Retained / Generated. % Burn-up at. % 500 ℃ 700 ℃ 900 ℃ 1 25 25 10 2 14 22 5 3 13 23 7	55
Li transport, g / h	$W = (29.9/2)\, F\, [K \cdot P(H_2O)]^{0.5} / P(\mathrm{total})$ F = He sweep gas flow rate (mol / h) $K = [P(LiOH)]^2 / P(H_2O)$, equilibrium constant for $Li_2O(s) + H_2O(g) \rightarrow 2\,LiOH(g)$ $P(H_2O)$ = water vapor pressure in atm. P (total) = total sweep gas pressure, atm.	56 57
Thermal conductivity	Slight decrease at low temp. due to fast neutron irradiation	58
Young's modulas	No data	
Compressive strength	No data	
Bending strength	No data	
Tritium diffusivity, cm^2 /s	$D = 4.03 \times 10^{-2} \exp[-95.1\,(\mathrm{kJ/mol}) / RT]$ $573 \leqq T \leqq 1173$ K, $R = 8.31 \times 10^{-3}$ kJ / m-K Single crystal diffusivity decreases with irradiation	59
Tritium residence time, h	$\tau = \exp(2.273 \times 10^4 / T - 34.83)$, He + 0.1 % He purge dg ~ 16 μm, p ~ 20 %, $593 \leqq T \leqq 773$ K,	60

1.2 Miscellaneous effects

Item	Data	Refs.
Effects of thermal cycling on strength	Performed extremely well. Pebble dia. 1 mm, 92 % T.D., 42 μm grain size, 400 – 800 ℃ heating –cooling rate of 20 ℃ /s, Up to 2000 cycles.	63

2. β Li_2TiO_3

2.1 Irradiation effects

Item	Data	Refs.
Physical integrity	No data	
Thermal properties	No data	
Mechanical properties	No data	
Swelling	No data	
Helium retention	Retained fraction, % (1 K/min ramp rate) Burn-up, at. % 673 K 773 K 873 K 0.007 78 10 4	61
Tritium diffusivity	No data	
Tritium residence time, h	Roughly similar to Li_2ZrO_3	****
U.S. Class C waste disposal rating	0.2 at 15 MW. yr / m^2 fluence, 10 - yr cooling	62
Afterheat, W / cm^2	0.05 at 15 MW. yr / m^2, 1 - hr cooling, 85 % dense	62
Tritium release	Tritium release performance is excellent and is similar to Li_2ZrO_3. More than 80 % tritium released within ~ 11 hr. at 250 ℃ (see Fig. 4-1, 4-2).	6 63 64

****: 6, 21, 60, 61, 63, 64

2.2 Miscellaneous effects

Item	Data							Refs.
Effects of thermal cycling on strength of Li_2TiO_3 sphere in 1.2 mm size. Compressive strength, N		Number of thermal cycles						63
	Sample	0	3	6	9	12	15	
	77.6 % T.D. 4 ~ 10 μm grain size	40.9	44.9	43.1	42.7	42.3	42.7	
	81.3 % T.D. 40 ~ 140 μm grain size	35.6	4.4	9.8	33.4	32.5	31.1	

Note: 1. Thermal cycle; 273 K→ 1273 K at 200 K / hr.

2. Li_2TiO_3 pellets behavior is expected to be similar to that of Li_2ZrO_3 pellets and that is excellent under ~ 30000 cycles.

3. Li_2ZrO_3

3.1 Irradiation effects

Item	Data	Refs.
Physical integrity	Very good	40
Swelling	Less than 0.7 %	40
Grain growth	No data	54
Li transport	No data	65
Thermal conductivity	No significant change	26
Thermal expansion	No significant change	26
Young's modulus	~ 30 % increase	26
Compressive strength	Significant decrease, not in agreement with bending strength behavior	26
Bending strength	Scattered values available	26
Helium retained	Very low	55
Tritium diffusivity	No single crystal data	
Tritium residence time, h	$\tau = 1.089 \times 10^{-19} \exp(230.5\ \mathrm{kJ}\ \square \mathrm{mol}^{-1} / RT)$, $T \geq 583$ K, $0.5 \leqq dg \leqq 1$ μm, $20 \leqq p \leqq 25$ % He + 0.1 % He purge	6 60

3.2 Miscellaneous effects

Item	Data		Refs.
Effects of thermal cycling	Pellet (83 % T.D.), 330 → 530 °C, 30 MPa, 1000 cycles	No fractured	68)
	Pebble (80 % T.D., 1 mm in size, 40 μm grain size)	Fractured significantly	

4. α Li_4SiO_4

4.1 Irradiation effects

Item	Data				Refs.
Physical integrity	Poor at 500, 700, 900 °C (< 3 at. % burn-up)				45,53
Swelling	$\Delta V / V_0$, %				47
	^{6}Li burn- up	500 °C	700 °C	900 °C	
	1	0.3	0.3	0.3	
	2	-	1.2	0.6	
	3	0.4	2.7	2.0	

Grain growth	At ~ 1 at. % ^{6}Li burn- up, none for 500 °C, 700 °C 1 → 2 μm at 900 °C	54
Helium retention	At 1 at.% ^{6}Li burn- up T, °C Retained / Generated, % 500 0.7 700 0.6 900 0.06	58
Tritium diffusivity, cm^2 /s	No single crystal data $D = 1.37 \times 10^{-7}$ exp (- 63 kJ / mol / RT) Based on grain size of polycrystalline samples	66
Tritium residence time, h	$\tau = 2.24 \times 10^{-7}$ exp (- 63 kJ□mol^{-1} / RT), dg ~ 20 μm, p ~ 0.08, $560 \leqq T \leqq 770$ K, He + 0.1 % He purge	67

4.2 Miscellaneous effects

Item	Data		Refs.
Effects of thermal cycling	Pebble (93 % T.D., 1 mm in size, 40 μm grain size), 400 – 800 °C, 20 °C / s, 50 cycles	Fractured significantly	68
	Pebble (80 % T.D., 0.4~0.6 mm in size, 40 μm grain size), 400 - 800 °C 20 °C / s, 50 cycles	Good performance	

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