富山大学水素同位体機能研究センター研究報告17：97－109，1997

トリチウム増殖材データベース (3)
Li_2TiO_3 固体増殖材

二村 嘉明
富山大学・水素同位体機能研究センター
〒 930-8555 富山市五福 3190 番地
河村 弘，土谷 邦彦
日本原子力研究所
〒 311-1394 茨城県東茨城郡大洗町成田新堀 3607

Breeding Material Data Base for Fusion Reactor (3)
(Li_2TiO_3 Solid Breeder)

Yoshiaki FUTAMURA
Hydrogen Isotope Research Center, Toyama University
Gofuku 3190, Toyama 930-8555, JAPAN
Hiroshi Kawamura and Kunihiko Tsuchiya
Japan Atomic Energy Research Institute
Shinbori 3607, Narita, Oarai-machi
Higashi-Ibaragi-Gun, Ibaragi 311-1394, JAPAN

ABSTRACT

This up-to-date compilation of data for lithium titanate, Li_2TiO_3, is part of a study to construct a database for breeding blanket of a fusion reactor, where existing data for breeding materials and neutron multipliers have been collected from as many literature as possible.

This compilation includes physical properties, thermal and mechanical properties, chemical stability and compatibility, tritium solubility and transport, irradiation effects, afterheat characteristics, thermal cycling effects, waste disposal and other miscellaneous properties of lithium titanate.

1. Introduction

A wide variety of data on the properties of reference materials is required to design the breeding blanket of a fusion reactor and to evaluate the blanket performance. Those data are physical, thermal and mechanical properties, chemical stability and compatibility with relating blanket materials, interaction with tritium, irradiation effects and other properties that are inherent in breeding material, cooling material, purging gas and so on.

However, some properties were extensively investigated by many research groups, while the others were done by only one group or not reported. Many requisite data are under exploration. Under such circumstances, however, it is significant to construct the data base which should be indispensable for designing the breeder blanket. From this viewpoint, the authors have collected and reviewed data reported for various breeding materials. As the first step of this effort, material data for Li_2O were compiled in our previous paper[1]. Similar compilation was made for Li_2ZrO_3 and Li_2TiO_2[2]. These reports have made it clear what kind of data is available, when and by whom the data were obtained. It was also recognized that relevant data for lithium titanate, Li_2TiO_3, are quite limited[2], in spite of its importance as an attractive alternate of Li_2O. The authors, therefore, have concentrated their effort to collect more data for this ceramic breeder material. This up-to-date compilation is supplementary to the our previous reports.

2. Data Collection and Arrangement

The material properties cited in this compilation were selected from collected papers and literature from a viewpoint of their importance for designing the breeder blanket and for the analysis of blanket performance. The authors, however, cited all of the reported values of a material constant or property, even if there is a considerable discrepancy between them. Those data appear in principle in order of publication.

3. Selected material properties

The primary functions of the breeding blanket are 1) tritium production by $n + {}^6Li \rightarrow T + {}^4He$ reaction and tritium release into purge gas, 2) heat generation and its transfer to liquid or gas coolant for power generation, 3) neutron shielding. Beside the properties relating to the above functions, other kinds of material properties are also quite important; they are chemical stability, compatibility and interaction with blanket materials, irradiation effects and so on.

In addition, the safety assessment requires such data as the irradiation effects, the waste disposal and afterheat characteristics. Moreover the effects of thermal cycling on strength of Li_2TiO_3 is an important material property. The items appearing in Table 3.1 are selected from the above mentioned viewpoint as primary important material properties for designing the blanket and the performance analysis.

Table 3.1 Data Item List of Ceramic Breeder Material(Li_2TiO_3)

Physical properties	Chemical stability and compatibility	Irradiation effects
・Crystalline structure ・Molecular weight ・Density ・Melting Point ・Thermal conductivity ・Thermal expansion ・Specific heat ・Heat capacityt ・Vapor pressure ・Pebble bed thermal conductivity	・Compatibility with water ・Compatibility with structure material ・Compatibility with Be ・Interaction with reprocessing liquid ・Interaction with acid Li dissolution	・Grain growth ・Swelling ・Physical integrity ・Li transport ・Thermal conductivity ・Thermal expansion ・Young's modulus ・Compressive strength ・Bending strength ・Helium retained ・Tritium diffusivity ・Tritium residence time ・Afterheat ・US Class C waste disposal rating ・Thermal cycling effect
Mechanical properties	**Tritium solubility and transport**	
・Young's modulus ・Poisson's ratio ・Tensile strength ・Comprssive strength ・Bending strength ・Rupture strength ・Crush strength ・Thermal creep rate ・Vickers hardness	・Li transport ・Titium diffusivity ・Hydrogen solubility ・Hydrogen adsorption ・Tritium solubility ・Tritium desorption ・Tritium release	

4. Data Representation

Tables below summarizes the data for selected material properties. The main parts of the tables are "Data", "Formula Expression" and "Remarks". The first one represents material constants, the second the variation of the properties with a given parameter, and the third the validity of the formula. In the case that experimental data points are available as function of a parameter which is mostly temperature, they are shown in Figures with calculated curves from the formula expression in a range from room temperature to the maximum temperature under the normal operation conditions. The presence of these figures are indicated in the column of "Reference Figure". In addition to the above, reference literature and papers are listed in the table, for readers convenience to investigate more detail the experimental methods, conditions, data precision, data analysis and so on.

Namely, the followings are given in Tables 4.1 ~ 4.5.

Item: selected property

Data number: ordinal number of data the source

Data: ( ) indicates the extrapolated value.

Unit: principally in C.G.S unit, otherwise the unit used in the source report

Formula Expression: parametric expression of the property by a selected variable

Range of Validity: applicable range of the formula; if necessary additional comments are given in this column as remarks

Reference Figure: diagrammatic presentation of the formula, or the source data

References: reference papers and literature

Table 4.6 summarizes author's observations of the effect of thermal cycling on compressive strength of lithium titanate spheres, where two types of spheres were examined. One was sintered at 1498 K for 4 hours, which is denoted as Sample No.1, the other at 1573 K for 4 hours, being denoted as Sample No.2. They were subjected to 15 thermal cycles from room temperature to 1273 K with a temperature ramp of 200 K/h. Sample No.1 appears to be suffered little degradation by thermal cycling. On the other hand, Sample No.2 was considerable degraded in several cycles, but recovered by further cycles to the as-sintered values. Those observations indicate that the Li_2TiO_3 spheres are inherently much more stable to thermal cycling than Li_2ZrO_3 spheres under similar conditions.

Table 4.1 Physical properties of Li_2TiO_3 (β)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.1.1 Crystalline Structure	1	Monoclinic					3), 4), 7)
	2	Monoclinic			Sintered at 1050℃ -3h 0.95 Li_2TiO_3 (monoclinic)		2)
4.1.2 Molecular Weight	1		g/g-mol	$109.93(1-1.82\times10^{-2}\delta)$			4), 7)
4.1.3 Density	1	2.0(α) 3.43(β) 2.57(γ)	g/cm^3		α=cubic, β=monoclinic, γ=cubic		1)
	2	3.43(β)	g/cm^3				2)
	3		g/cm^3	3.44(1-1.82×10-2δ)	δ=^{6}Li fraction in Li		4), 7)
4.1.4 Melting Point	1	1535	℃				1)
	2	1535	℃	Li/Ti=2.0, 100%T.D.			2)
	3	1535	℃				4), 7)
4.1.5 Li Density	1		g/cm^3	0.37δ for ^{6}Li, 0.44(1-δ) for ^{7}Li	δ=^{6}Li fraction in Li		4), 7)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.1.6 Thermal Conductivity	1	2	W/m-K		1000K, 85%T.D.		1)
	2	1.955	W/m-K		Li/Ti=1.9, 80%T.D.		2)
	3		W/m-K	$3.258(1-\varepsilon)$	monoclinic, ε=porosity (0.1~0.3)		-
	4		W/m-K	$(1-p)^2(3.55-2.26\times10^{3}T+1.51\times10^{-6}T^2)$	p=porosity, $0.18\leqq p\leqq 0.25$, $400\leqq T\leqq 1400K$	Fig.4.1	3), 8)
	5		W/m-K	$(1-\varepsilon)^{2.9}(5.35-4.78\times10^{-3}T+2.87\times10^{-6}T^2)$	ε=porosity, $0.14\leqq p\leqq 0.25$, $400\leqq T\leqq 1400K$	Fig.4.1	4)
4.1.7 Thermal Diffusivity	1	(Fig.4.3)				Fig.4.3	4)
4.1.8 Thermal Expansion	1	16×10^{-6}	1/K				1)
	2	21×10^{-6}	1/K		Li/Ti=1.9, 80%T.D. (linear)		2)
	3	1.2	%		Room Temp. ~ 700℃ (linear)		3)
	4		%	$-0.4119+1.154\times10^{-3}T+5.505\times10^{-7}T^2$	Linear expansion		3), 9)
	5		1/K	$1.154\times10^{-5}+1.101\times10^{-8}T$	Instantaneous Coeff.		3), 4)
	6		1/K	$(-0.4119+1.154\times10^{-3}T+5.505\times10^{-7}T^2)\div(T-273)$	Mean coeff., $373\leqq T\leqq 1073K$		3)
	7		1/K	$(-0.4119+1.154\times10^{-3}T+5.505\times10^{-7}T^2)\div(T-273)$	Mean coeff., $373\leqq T\leqq 1073K$		4)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.1.9 Specific Heat	1	1.0	kJ/kg-K		300K		1)
	2		kJ/kg-K	$0.64+0.0013T-5.0\times10^{-7}T^2$	$298\leqq T\leqq 1400K$		2)
	3		J/kg-K	$355(T-100)^{1.1}/(1+0.3T^{1.05})$	$300\leqq T\leqq 1400K$		
4.1.10 Heat Capacity	1	1428	J/kg-K		Li/Ti=1.9, 80%T.D.	Fig.4.2	4)
4.1.11 Vapor Pressure	1	No data	Pa		(under investigation)		1)
	2		K	$839+(305+87.3\log(100pD_2O)-78.3\log(pD_2)/(1+2.55\times10^{-10}\log(100pD_2O)^{11.6})$	Temperature at which total lithium vapor pressure is 0.001Pa. $10\leqq pD_2O\leqq 100Pa$ pD_2O=partial pressure of D_2		2)
4.1.12 Pebble Bed Thermal Conductivity	1		W/m-K	$(1-\varepsilon)(0.74+0.00015(T-273)+3.3\times10^{-7}(T-273)^2/0.52$	ε=porosity 0.7~1.2mm dia. pebbles, 0.1MPaHe, $300\leqq T\leqq 1300K$, $0.43\leqq \varepsilon\leqq 0.48$		3)
	2		W/m-K	$0.47+5.5\times10^{-4}T$	1.2mm pebbles, 82% dense., 63% packing fraction, 0.1MPaHe, $300\leqq T\leqq 1300K$		3), 9)

Table 4.2 Mechanical properties of Li_2TiO_3 (β)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.2.1 Young's Modulus	1	123.3	GPa	$266(1-\varepsilon)(1-1.2\varepsilon)^2$	Li/Ti=1.9, 80%T.D. (ε=0.2) ε=porosity		2)
	2		GPa	$266.8(1-\varepsilon)(1-1.2\varepsilon)^2$	$0.1\leqq\varepsilon\leqq0.3$, 300K 1.2μm grains		4)
4.2.2 Poissons's Ratio	1			$0.3(1-\varepsilon)$	$0.1\leqq\varepsilon\leqq0.3$, 300K		2), 4)
4.2.3 Tensile Strength		No data			(under investigation)		
4.2.4 Compressive Strength		No data			(under investigation)		
4.2.5 Bending Strength	1	60	MPa	$3.44(1-1.82\times10-2\delta)$	300K, 85%T.D., 10 μm grains		3)
4.2.6 Rupture Strength	1	92	MPa	$170(1-2.27\varepsilon)$	Li/Ti=1.9, 80%T.D., (ε=0.2)		2)
	2		MPa	$170(1-2.27\varepsilon)$	$0.1\leqq\varepsilon\leqq0.3$, 300K 1.2μm grains		4)
4.2.7 Crush Strength	1	30	N		4~10 μm grains, 85% dense. 1.2mm pebbles (weibull)		3), 4) 13), 14)
	2	40	N		40~140 μm grains, 78% dense. 1.2mm pebbles (weibull)		3), 4) 13), 14)
	3	40	N	0.37δ for ^6Li, $0.44(1-\delta)$ for ^7Li	~20 μm grains, 67% dense. 1.6mm pebbles (mean)		4)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.2.8 Thermal Creep Rate		No data	1/s		(under investigation)		
4.2.9 Vickers Hardness	1	192	MPa	363(1-2.36ε)	80%T.D., ε=0.2		2)
	2		1/K	363(1-2.36ε)	0.1≦ε≦0.3, 300K		4)

Table 4.3 Chemical stability and compatibility of Li_2TiO_3 (β) (Interaction with other material)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.3.1 Compatibility with Water	1	Excellent		No interaction with water. Difficult soluble in water. No dissolution of Li is detectable after 40 days immersion.			2)
	2	Low solubility in water		<< 1% uptake after 6 month exposure to room air.	<<1% uptake after 6 month exposure to room air.		4)
4.3.2 Compatibility with Structural Material (steel)	1			A very extremely small amount of interaction with 316SS, HT9 and 316SS+Ni at 600℃.	Temperature range used is 400~820℃.		1)
	2	<7 (steel)	μm		Steel reaction layer 500℃, 10^4h, 10Pa H_2O		3)
	3			No compatibility concern with steels.	~800℃		2)
	4		μm	$3600t^{0.5}exp$ (-9000/T)	316SS. Penetration depth 0.1MPa He, 823≦T≦923K, 410≦t≦1023h		3), 4), 8)
4.3.3 Compatibility with Be		No data			(under investigation)		
4.3.4 Interaction with Reprocessing Liquid				90%Li recovery after refluxing in 95% aqua-regia+5%HF for 4 h.			3), 13)
4.3.5 Interaction with Acid : Li Dissolution				90%Li after 4 h in 95% aqua-regia+5%HF. 84% after 15 h in 1M HNO3 at 323K.			4)

Table 4.4 Tritium solubility and transport of Li_2TiO_3 (β)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.4.1 Li Transport		No data			(under investigation)		
4.4.2 Tritium Diffusivity	1	~10^{-9}	cm^2/s		600℃		1)
	2	5.16	10^{-7} m^2/s	6.455(1-ε)	Li/Ti=1.9, 80%T.D. (ε=0.2) (Thermal diffusivity)		2)
	3	Not available					3), 4)
4.4.3 Hydrogen Solubility				≦3×$10^{-7}exp$ (+3600/T) mol•fr/Pa	Interaction with hydrogen 573≦T≦773K, 2~100kPa		3), 4)
4.4.4 Hydrogen Adsorption		No data			(under investigation)		3), 4)
4.4.5 Tritium Solubility		No data			(under investigation)		
4.4.6 Tritium Desorption		Fig. Expression				Fig.4.4.2	16)
4.4.7 Tritium Release	1	Fig. Expression			Release rate rapid by increases when heated from 200℃ to 250 ℃.	Fig.4.4.1	17)
	2	Fig. Expression				Fig.4.4.3	15)
	3	Fig. Expression				Fig.4.4.4	17)

Table 4.5 Irradiation effects of Li_2TiO_3 (β)

Item	Data No.	Data	Unit	Data of Formula Expression	The Range of Validity or Remark	Reference Figure	References
4.5.1 Grain Growth		No data			(under investigation)		
4.5.2 Swelling		No data			(under investigation)		
4.5.3 Physical Integrity		No data			(under investigation)		
4.5.4 Li Transport		No data			(under investigation)		
4.5.5 Thermal Conductivity		No data			(under investigation)		
4.5.6 Thermal Expansion		No data			(under investigation)		
4.5.7 Young's Modulus		No data			(under investigation)		
4.5.8 Compressive Strength		No data			(under investigation)		
4.5.9 Bending Strength		No data			(under investigation)		
4.5.10 Helium Retained		78 (673K) 10 (773K) 4 (873K)	%		% : (Retained)/(Generated) 1K/min, ramp rate Burn up atom % : 0.007		3), 4), 5)
4.5.11 Tritium Diffusivity		Not Available			(under investigation)		4)
4.5.12 Tritium Residence Time	1	<1	h		1 μm grains, 400℃, 80%T.D.		3)
	2			Roughly similar to Li_2ZrO_3			4)
4.5.13 After Heat		0.05	W/cm^3		$15MW{\cdot}yr/m^2$, 1 h cooling, 85% dense, 2~100 times lower than Li_2ZrO_3		4)
4.5.14 US Class C Waste Disposal Rating		0.17			More than 10 times lower than Li_2ZrO_3. $15MW{\cdot}yr/m^2$, 10yr cooling		3), 4), 6)

Table 4.6 Effect of thermal cycling on strength of Litium titanate spheres

Samples	Compressive strehgth	Number of thermal cycles					
		0	3	6	9	12	15
No. 1 sample 1498 K/4h	Strength(N)	40.9	44.9	43.1	42.7	42.3	42.7
	Weibull modulus	7.4	4.7	5.4	4.7	4.0	5.3
No. 2 sample 1573 K/4h	Strength(N)	35.6	4.4	9.8	33.4	32.5	31.1
	Weibull modulus	4.4	4.1	2.3	4,4	3.2	3.8

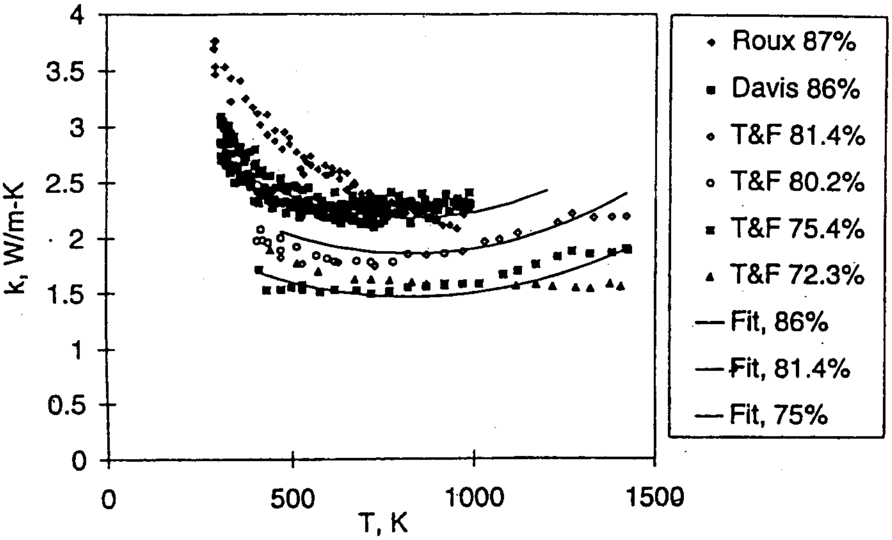

Fig.4.1 Thermal conductivity data for Li_2TiO_3. The curved lines[2),12),17)] are from the fit given in Table 4.1.

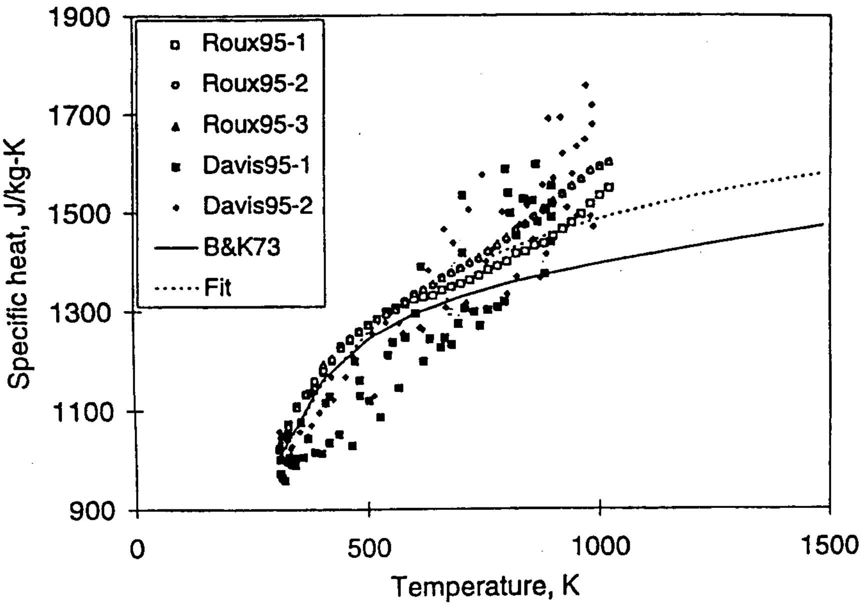

Fig.4.2 Specific heat data for Li_2TiO_3. The dashed curve is the[2),12)] fitting equation given in Table 4.1.

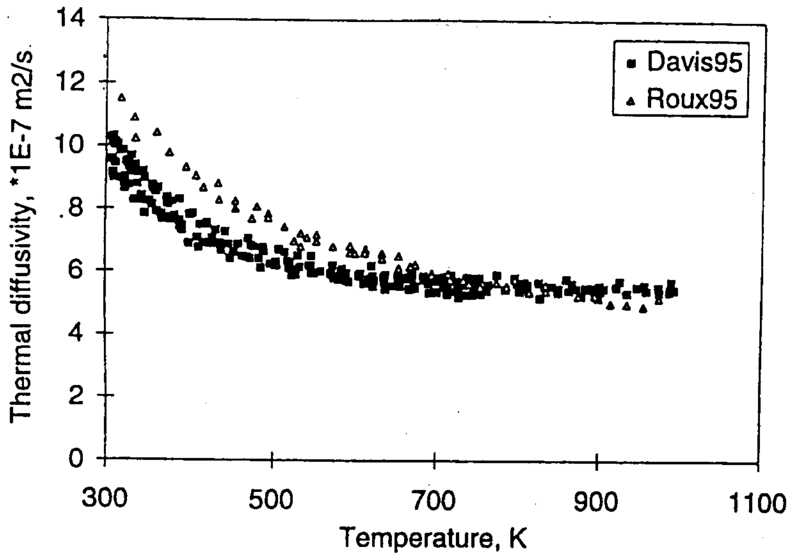

Fig.4.3 Measured thermal diffusivity of 87% dense Li_2TiO_3. The [2),12)] values for each group are an overlay of two or three separate runs.

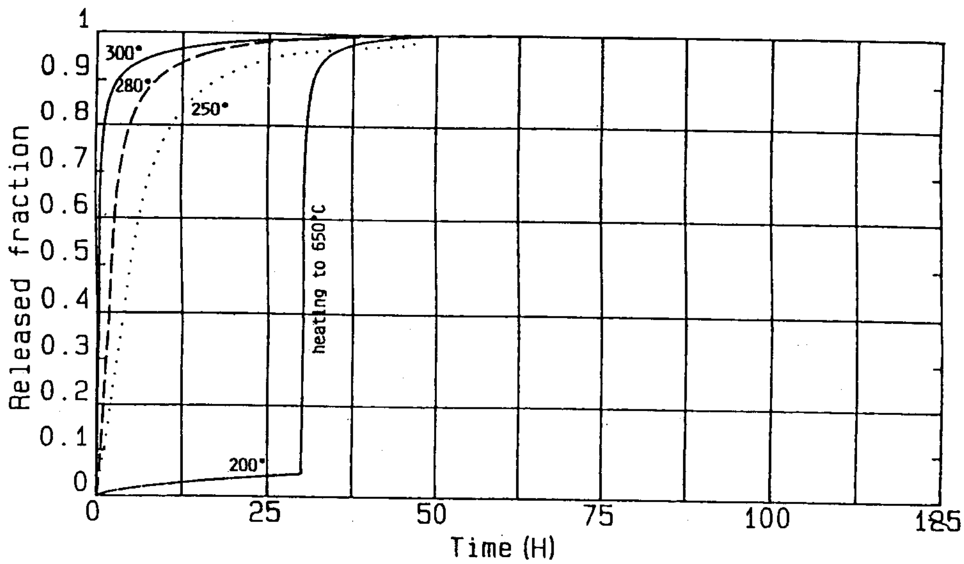

Fig. 4.4.1. Isothermal tritium release at 300℃, 280℃, 250℃, 200℃ in He + 0.1% H_2 purge gas, flowrate 2.4 lh^{-1} for Li_2TiO_3 [2)].

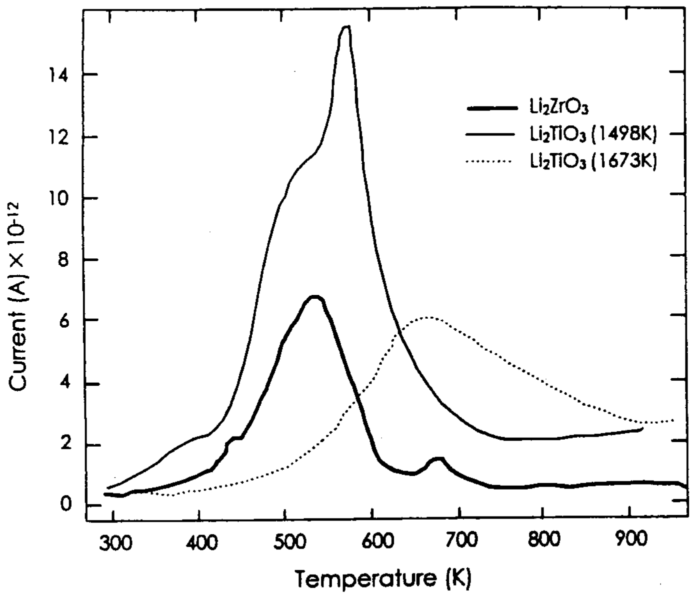

Fig. 4.4.2. Tritium desorption curves for Li_2ZrO_3 and Li_2TiO_3 at a linear heating rate of 2 K/min, pure He sweep gas[13),16)].

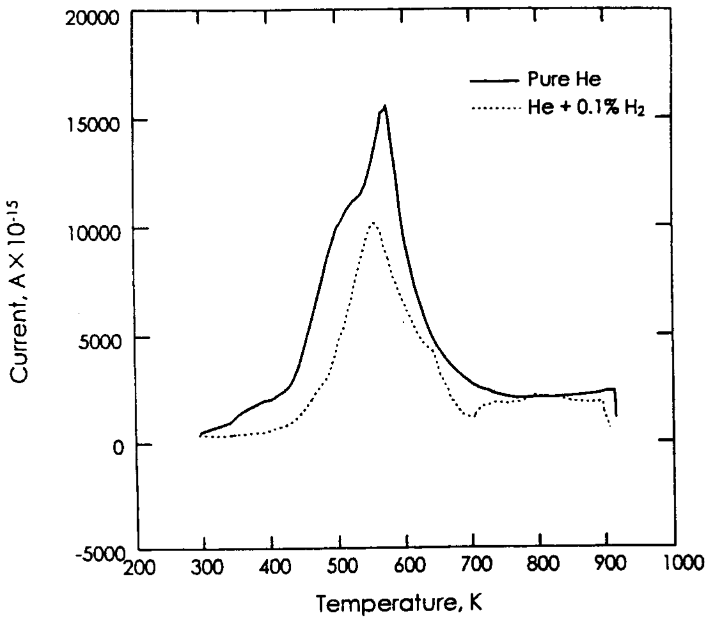

Fig.4.4.3. Effect of purge gas composition on tritium release from[17)] sample sintered at 1498K and heating rate of 2K/min. (Li_2TiO_3)

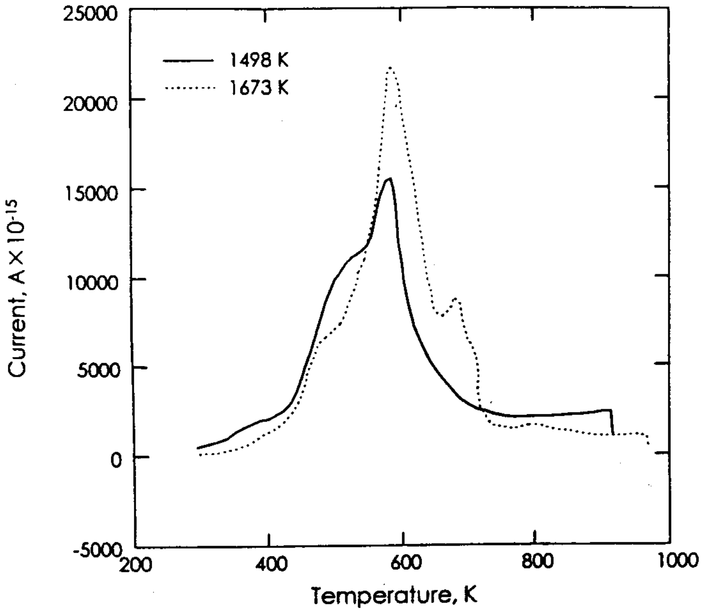

Fig.4.4.4. Effect of sintered temperature on tritium release for a [17] purge gas of pure helium and heating rate of 2K/min. (Li_2TiO_3)

5. Concluding Remarks

In this compilation, the authors did not review and evaluate the collected data on the properties of Li_2TiO_3. This is because that there might be still some oversight of existing data which are believed to be important, and hence it is premature to make review and evaluation. From this viewpoint, the authors will continue to direct their efforts to collect relevant data not only for Li_2TiO_3 but also other candidates of breeding materials, neutron multiplies, construction materials, cooling and so on.

However, owing to the limitation of our research and searching 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.

References

1) Y.Futamura, K.Horii and H.Kawamura, Ann. Rept. Hydrogen Isot. Res. Ctr., Toyama Univ., 15 (1995) 85

2) Y.Futamura and H.Kawamura, Ann. Rept. Hydrogen Isot. Res. Ctr., Toyama Univ., 16 (1996) 93

3) Nuclear Fusion Special Study Summary Group, "Evaluation Study on the Breeding and Recovery Characteristics of Tritium Breeding Material for Fusion Reactor", 1983

4) N. Roux, J.Avon, A.Floreancing, J.Mougin and S.Ravel, "Low Temperature Tritium Release Ceramics as Potential Materials for the ITER Breeding Blanket", Proc. Int. Workshop on Ceramics Breeder-Blanket Interactions, Oct. 9-11, 1995, Kyoto, Japan

5) P.Gierszewski, "Review of Porperties of Lithium Metatitanate", CFFTP G-9561, Oct. 1995

6) P.Gierszewski, "Review of Properties of Lithium Metatitanate", CFFTP G-9703, April, 1997,

7) J.Mougin, B.Rasneur and N.Roux,"Tritium and Hellium Release from Li2tiO3 comparison with Li2ZrO3", Proc. 3rd Int. Workshop on Ceramic BreederBlanket Interactions, Los Angels, U.S.A., 1994

8) M.A.Abdou, A.H.Hadid and A.R.Raffray, "Modeling analysis and Experiments for Fusion Nuclear Technology",Fusion Engn. Design, 6 (1988) 3

9) D.J.Suiter, "Lithium Baseoxide Ceramics for Tritium Breeding Applications", McDonnel Douglas Astronatics, MDCE 2677, June, 1983

10) P.Finn, T.Kurasawa, S.Nau, K.Noda and H.Watanabe, "Solid Oxide Compounds Properties necessary for Fusion Applications", Proc. IEEE 9th Symp. on Engineering Problems of Fusion Research (Chicago, 1981), Vol. II, 1200

11) R.T.Girad, C.T.Sims and H.R.Wisely, "Protective Ceramic Coating", US Patent 3,397,080, (13 Aug. 1968)

12) A.Christensen, K.C.Conway and K.K.Kelley. "High Temperature Heat Content and entropies of Aluminates and Ferrites of Lithium, Sodium and of Lithium Titanate", US Bur. Mines Rept. RI-5565 (1960)

13) M.Yamawaki, A.Suzuki, M.Yasumoto and K.Yamaguchi, "Proc. 5th Int. Workshop on Ceramic Breeder Blanket Interactions", Rome, 1996

14) J.Davis and A.Haasz, J. Nucl. Mater., 232 (1996) 65

15) P.Gierzewski, H.Hamilton, J.Miller, J.Sullivan, R.Verael and J.Earnshaw, Fusion Engn. Design, 27 (1995) 297

16) H.Hamilton, J. Nucl. Mater., 219 (1995) 274

17) J.M.Miler, H.B.Hamilton and J.d.Sullivan, J. Nucl. Mater., 212/215 (1994) 877

18) J.P.Kopasz, J.M.Miller and C.E.Johnson, J. Nucl. Mater., 212/215 (1994) 927

19) K. Watanabe, M. Matsuyama, T. Kobayashi, and S. Taguchi. Gas chromatographic separation of h_2-d_2 mixtures by Pd-Pt alloy near room temperature. *J. Alloys and Compounds,*, p. in press, 1997.