CONF-900634--3

DE90 013672

CERAMIC BREEDER MATERIALS

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The breeding blanket is a key component of the fusion reactor because it directly involves tritium breeding and energy extraction, both of which are critical to development of fusion power. The lithium ceramics continue to show promise as candidate breeder materials. This promise was recognized by the International Thermonuclear Reactor (ITER) design team in its selection of ceramics as the first option for the ITER breeder material. Blanket design studies have indicated properties in the candidate materials data base that need further investigation. Current studies are focusing on tritium release behavior at high burnup, changes in thermophysical properties with burnup, compatibility between the ceramic breeder and beryllium multiplier, and phase changes with burnup. Laboratory and in-reactor tests, some as part of an international collaboration for development of ceramic breeder materials, are underway.

1. INTRODUCTION

The development of ceramic breeder materials has progressed systematically in laboratory experiments, in-reactor testing, and tritium transport and release modeling. These efforts have resulted in development of a broad properties data base for several materials in differing configurations (i.e., sintered pellets, pebbles, single crystals).[1,2] The lithium-containing ceramics (Li_2O, γ-$LiAlO_2$, Li_4SiO_4, and Li_2ZrO_3) are considered to have excellent potential as tritium breeders because of the ease of tritium recovery, excellent thermal performance, and good irradiation behavior. Also, these efforts have indicated that optimum information on materials performance is obtained when a candidate material is tested in a fashion that results in multiple effects taking place (gas production, atomic recoil, and tritium production, release, and recovery).

Current experimental research is addressing issues identified in blanket design studies, for example, compatibility of the breeder with the beryllium multiplier, tritium release behavior at high burnup, effects of breeder burnup on thermophysical properties, and operation at lower temperatures (i.e., <623 K). At present, the design studies place a great emphasis on neutron irradiation effects, and the experimental effort reflects interest in multiple effects. However, complementary separate-effects laboratory experiments are still required to ensure correct interpretation of a material's irradiation behavior. This paper will focus on recent research concerning candidate materials properties, fabrication methodology, irradiation behavior, and tritium transport, as well as computer modeling of tritium transport and release.

2. MATERIALS PROPERTIES

The current properties data tabulations for candidate ceramics are based on comparative measurements from various studies;[3-6] a rigorous comparison and assessment of candidate materials can only be achieved using values measured under comparable conditions and on comparable specimens. The impact of microstructure and impurities on materials properties, stability, and performance of ceramics has long been recognized.[7] For example, porosity, pore morphology, and grain size have profound effects on thermal conductivity, mechanical performance, stability, and tritium inventory. Impurities can affect thermodynamic and chemical properties as well as transport behavior.

Table I lists the melting point (T_m), lithium atom density (ρ_{Li}), bulk density (ρ_{TD}), thermal conductivity (K), thermal expansion (α), Young's modulus (E), and a performance parameter ($K/E\alpha$) that assesses resistance to thermal crack initiation. High lithium atom density, high thermal conductivity, broad operating temperature range, and low tritium solubility are all favorable qualities. Among the candidates lithium oxide is highly regarded because of its high lithium atom content, low tritium solubility, high thermal conductivity, reasonably rapid tritium release, and potential for high tritium recovery. In addition, it has the highest tritium breeding ratio relative to the other candidates. Its principal disadvantage results from a high hydroxide/trioxde and atomic lithium vapor pressure, which could result in transport of lithium to cooler zones of the blanket. Lithium aluminate might be considered superior to Li_2O because of its better swelling resistance, higher melting point, broader operating temperature window, slow reaction with water, and excellent irradiation behavior, especially for high density material (95% T.D.). However, because its tritium release characteristics are poorer, $LiAlO_2$ requires a higher minimum operating temperature to maintain low tritium inventory. Li_4SiO_4 behaves much like Li_2O in many respects. It exhibits good tritium diffusivity and chemical stability. However, recent closed capsule irradiation tests showed this material to fragment severely, probably due to differential thermal expansion.[15] While Li_2ZrO_3 has exhibited excellent stability, low tritium retention, and excellent tritium release behavior, its principal disadvantage is activation of zirconium, resulting in decay heat after shut down.

Table 1 Data on Several Properties of Candidate Breeder Materials

Breeder	T_m, K	ρ_{Li}, g/cm^3	ρ_{TD}, g/cm^3	K, W/(m•K)	α, 10^{-5}/K	E, GPa	K/E•α, 10^{-6}m^2/s
Li_2O	1706	0.93	2.01	4.4	3.3	141	9.7
$LiAlO_2$	1883	0.27	2.61	2.3	1.2	210	9.1
Li_4SiO_4	1523	0.54	2.35	2.3	2.0	85	13.5
Li_2ZrO_3	1888	0.33	4.15	2.2	1.1	160	7

Transformation of materials during neutron irradiation must also be considered because the neutron capture process eliminates one chemical component (Li) and produces two others (T, He). These compositional changes can lead to the formation of second phases either as internal precipitates or as solid solutions. A change in composition for a ternary oxide is likely to result in changes in its properties, e.g., melting point, tritium diffusivity, and thermomechanical performance. Further, in any detailed evaluation of candiidate blanket breeder materials, strong consideration must be given to their tritium breeding potential. Currently, blanket designs use beryllium for neutron multiplication to ensure an adequate tritium breeding ratio (tritium atoms produced per fusion neutron).

3. MATERIALS PREPARATION AND FABRICATION

For material preparation and fabrication, two steps are considered: a) preparation of the powder by chemical conversion of a commercially available source material (Li_2CO_3 or LiOH) into the desired oxide and b) the compaction of the powder to the desired shape. The preparation of sinterable powders from Li_2CO_3 and LiOH source material characteristically follows "dry" ball milling procedures or "wet" processes. The wet processes avoid introduction of impurities in the course of the dry milling step. In the dry process, an oxide powder (e.g., Al_2O_3, SiO_2, ZrO_2) and lithium carbonate are ball-milled together and heated to ~700°C. At this temperature a slow reaction leads to the formation of the lithium-containing ternary oxide. Control of grain size and porosity is obtained by adjustments in the mixing ratio of starting materials and sintering temperature.[8] In an alternative wet process, a LiOH solution is slowly fed into a highly dispersed aqueous suspension of the oxide. A final spray drying and calcining step at 600°C leads to a sinration of the Li_2O, several methods are applicable. In a typical process, the source material (Li_2CO_3) is calcined in vacuum and ball milled to a sinterable powder.[10] Another process starts with an aqueous solution of LiOH followed by precipitation of the peroxide (Li_2O_2) with H_2O_2. This precipitate is converted to a sinterable Li_2O powder by vacuum calcining at 300°-400°C.[11]

The quality of a sinterable powder is primarily defined by its specific surface area. For example, ceramic produced by spray-drying is easily processed to yield homogeneous compacts.[12] To obtain open pore structures, further preparational steps like granulation and subsequent calcination are necessary.

For compaction of the ceramic powder to shaped solids, different procedures are applicable, especially a) cold-pressing and sintering, b) precompacting and hot isostatic pressing, c) extrusion, granulation, and sintering, and d) melting, liquid drop formation, and solidification. The simple procedure of cold-pressing and sintering is commonly used in mass production of ceramic materials. The sintering temperature varies between 800° and 1100°C and is an important factor for controlling the pellet structure. The sintering time is on the order of five hours, depending on the preconditioning of the powder. Hot pressing in a temperature range between 500° and 900°C may lead to compacts of very high density. In this more expensive process, the original grain size of the powder will not increase due to the lower temperature and the short exposure time.[13]

The fabrication of spherical particles can be carried out by the granulation of extruded materials. Ideal spherical shapes could be obtained by melting and freezing. However, free flowing particle beds are normally desired because they can be formed satisfactorily using "pebbles" of irregular size.

4. IRRADIATION BEHAVIOR

Lifetime testing of the ceramic breeder materials is required to evaluate materials behavior at long burnups and under large temperature gradients. The low cross section of ^6Li for high energy neutrons (>1 MeV) results in an almost homogeneous reaction throughout the breeder sample. This "global" effect then leads to high internal heat generation and development of large differences in temperature between the center and edge of the sample. Such experiments can provide an approximation of operating a ceramic breeder material under reactor-like conditions. The FUBR series of irradiations[14-16] is an example of testing in a fast reactor, while the ALICE series of irradiations[17]

The FUBR tests indicate that tritium retention is lowest for Li_2ZrO_3 and highest for $LiAlO_2$ and that helium retention follows a similar order. However, Li_2O has a high retention of helium at high burnup and low temperature (<773K). In the FUBR tests, Li_4SiO_4 showed a tendency for fragmentation as compared with $LiAlO_2$ and Li_2O, while Li_2ZrO_3 remained relatively crack free during irradiation. Fragmentation was not burnup dependent and was thought to result from thermal stresses arising from thermal gradients and thermal expansion.[15] In the ALICE experiments,[17] no significant fragmentation of $LiAlO_2$ was observed up to 873 K and 1 at.% burnup; severe fragmentation was observed at 1023 K with thermal gradients at 80 K/mm.

In the FUBR 1A experiment, swelling at 973 K and 1173 K was observed to be very low for $LiAlO_2$ (85% T.D.) and Li_2ZrO_3, slightly lower for Li_4SiO_4, and rather high for Li_2O. Swelling was thought to arise from the retained helium in the material.[18] A small shrinkage was observed (<0.03%) for 75% T.D. $LiAlO_2$ in the ALICE 2 experiment.[17] Significant changes were noticed in grain growth for Li_2O, a slight growth for Li_4SiO_4, and no change for $LiAlO_2$ and Li_2ZrO_3.[18]

The thermal conductivity of irradiated Li_2O and $LiAlO_2$ has been investigated by Ethridge[19] in the temperature range 373-1173 K. Samples were irradiated at 773-1173 K to lithium burnup of 11.5×10^{20} captures/cm^3. In general, the measured conductivity of the irradiated material was quite similar to that for non-irradiated material. Reductions in thermal conductivity at temperatures <573 K were observed for lithium oxide samples as a result of irradiation-induced lattice damage, whereas at temperatures >573 K the thermal conductivities approached values well within the error band of non-irradiated lithium oxide. This is consistent with the general expectation that at higher temperatures the annealing of irradiation-induced defects would improve thermal conductivity. The thermal conductivity of irradiated lithium aluminate samples remained relatively constant with temperature for all irradiation times and temperatures and was only slightly lower than that of non-irradiated $LiAlO_2$ at low temperatures (<700 K, see Figure 1). Botter et al.[17] reported that $LiAlO_2$ samples showed no measurable change of thermal conductivity after irradiation in OSIRIS to 1% burnup at 873 K and 2% burnup at 1073 K.

No significant change of Young's modulus for $LiAlO_2$ specimens was observed after irradiation to 1% burnup at 673 K; a slight decrease was measured at 873 K.[17] An increase in Young's modulus, correlated to specimen shrinkage was, observed in irradiations up to 123 K and 2% burnup.[18] Changes in compressive strength were investigated after irradiation in the ALICE 1 and 2 nonirradiated $LiAlO_2$.

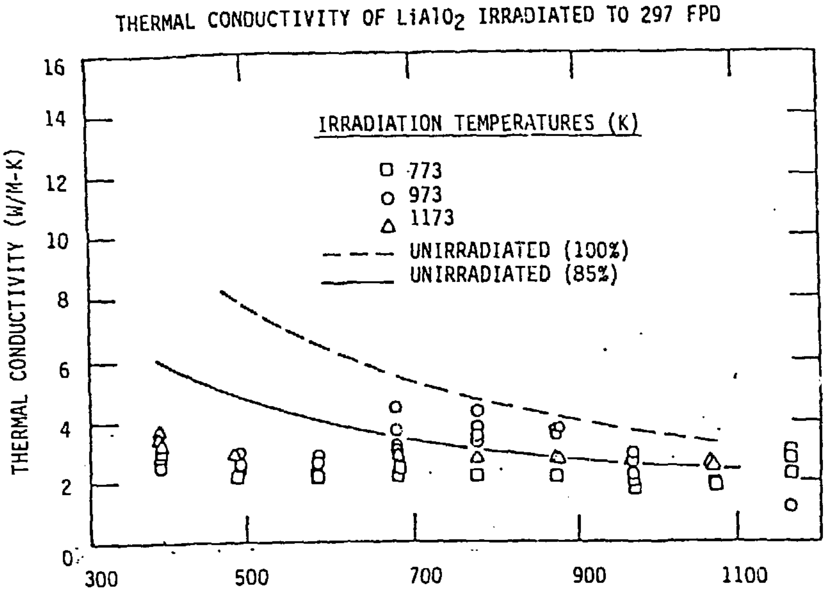

FIGURE 1
Thermal conductivity of irradiated $LiAlO_2$ as function of conductivity-measurement temperature. The dashed line represents 100% T.D. $LiAlO_2$ while the solid line is for 85% T.D. $LiAlO_2$, which is comparable with the irradiated material.

5. METHODS FOR ENHANCED TRITIUM RELEASE

The solid-state defect structure of the ceramic (lithium vacancy, defects, traps, etc.) can strongly influence the tritium transport and release process. The origin of the lithium vacancy (V_{Li}) can arise from (1) the $^6Li(n,\alpha)T$ reaction, which generates many defects in transforming Li into ^3H and ^4He atoms, (2) defects created by displacement damage, i.e., recoil of energetic ^3H and ^4He atoms, and (3) the extrinsic impurity-induced defects that control lithium diffusion.

To permit lower temperature operating conditions for solid breeders, nonthermal methods of increasing tritium transport and release need to be developed. Adding small amounts of hydrogen into the helium purge gas stream has

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proven to be useful in increasing tritium release. For various design scenarios, however, further increase is desirable. Impurity/defect-induced increase of tritium release may represent a viable method of meeting this goal. In fact, existing experimental tritium release data from Li_2O have indicated a correlation between lithium and tritium transport.[20-21] Furthermore, impurity/defect-induced increase of the hydrogen transport (as an impurity) in a number of non-lithium oxides has been observed.[22-23] The presence of certain impurities may affect tritium diffusion by changing (1) the local concentration of free vacancies, (2) the activation energy and jump frequency of lattice atoms due to electronic effects, or (3) the correlation factor for diffusion by increasing the ratios of jump frequencies near impurities. Solids modification in which Li^+ ions are substituted with Mg^{2+} ions appears an appropriate testing scheme for increasing the vacancy concentration and thereby enhancing tritium transport and release.

5. MODELING TRITIUM TRANSPORT AND RELEASE

In an operating fusion reactor, the tritium breeding blanket will reach a steady state in which the tritium release rate equals the production rate. The tritium release rate must be sufficient to ensure that the tritium inventory in the blanket does not become excessive. The kinetics that govern the transport and release of tritium from the breeder material must be fully understood if we are to establish optimum operating temperature limits for the blanket. Tritium generated within a candidate material likely follows the mechanism a) diffusion to the grain surface, b) surface diffusion, c) surface reaction, d) desorption from the grain surface, and e) percolation through the pore structure.[24-25] Thus, parameters that must be modeled include tritium diffusion within the solid and desorption from the grain surface.

A model developed at ANL[26] considers diffusion and desorption as rate-controlling mechanisms for tritium release from a ceramic breeder. At the temperatures of interest, percolation in the gas phase and grain boundary diffusion should be orders of magnitude more rapid than diffusion in the grain. Desorption is included as a rate-limiting mechanism based on (1) the observations of desorption-controlled kinetics in some release experiments, and (2) the results of experiments in which the importance of surface reactions was identified by changing the hydrogen concentration in the helium purge gas. Diffusion is included as a mechanism based on the observation of diffusion-limited release.

The desorption activation energy is not constant but is dependent on the hydrogen surface coverage. Desorption activation energies which are dependent hydrogens will affect the binding energy of the hydrogen to the surface and, therefore, the desorption activation energy.

Model calculations have suggested three types of release behavior associated with a temperature change in the region where the desorption activation energy changes.[32] The type of behavior observed is dependent upon the magnitude of the change in desorption activation energy. When the change in the activation energy is relatively small, an increase in sample temperature results in the normal tritium release, i.e., an increase followed by decay to steady state. When the change in the desorption activation energy is large, an increase in sample temperature results in a decrease in tritium release followed by a slow rise to steady-state release. This type of behavior was observed in early tests of CRITIC.[31] The third type of behavior is for intermediate changes in the activation energy. For such changes, the calculated behavior with the ANL model is similar to the unusual behavior observed in the CRITIC experiment, i.e., an increase in sample temperature results in a sudden decrease in tritium release followed by an increase to a maximum, then decay to steady state. A characteristic example is illustrated in Fig. 2, which plots the tritium release calculated from the ANL model with that observed in the CRITIC experiment for a temperature increase from 435 to 615°C.

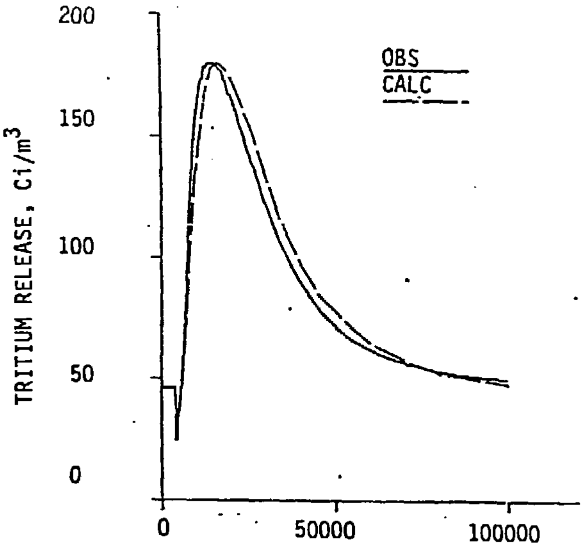

FIGURE 2
Calculated and Observed Tritium Release
for a Temperature Increase from 435 to 614°C.

REFERENCES

1) C. E. Johnson, K. R. Kummer, and E. Roth, J. Nucl. Mater. 155-157 (1988) 188-201.

2) C. E. Johnson, G. W. Hollenberg, N. Roux, and H. Watanabe, Fusion Eng. Design 8 (1989) 143-153.

3) D. Suiter, "Lithium Based Oxide Ceramics for Tritium Breeding Applications," Report MDC E 2677 (June 1983).

4) W. Dienst, "Properties and Comparison of Ceramic Oxide Breeder Materials for Fusion Reactors," this conference.

5) C. Denuziere and N. Roux, "Data and Properties of Aluminate $LiAlO_2$," CEA/NET Contract No. 161/84-5/FU-F/NET (November 1984).

6) A. Skokan, H. Wedemeyer, D. Vollath, and E. Gunther, Proc. 14th Symposium on Fusion Technology, Avignon, 1986 (Pergamon Press, Brussels, 1986), p. 1255.

7) W. D. Kingery et al., Introduction to Ceramics, 2nd ed. (John Wiley and Sons, New York, 1976).

8) E. Roth et al., Transactions ENC '86, Vol. 3, p. 145 (1986).

9) D. Vollath and H. Wedemeyer, J. Nucl. Mater. 141-143 (1986) 334.

10) R. M. Arons, R. B. Poeppel, M. Tetenbaum, and C. E. Johnson, J. Nucl. Mater. 103-104 (1981) 555.

11) P. Kennedy, K. E. Gilchrist, D. E. Walker, and S. Broughton, Fusion Techn. 2 (1986) 1013.

12) D. Vollath, H. Wedemeyer, and E. Gunther, J. Nucl. Mater. 131-134 (1985) 221.

13) F. Rigby and P. Kennedy, Fusion Techn. 2 (1984) 953.

14) G. W. Hollenberg, HEDL-7643 (1987).

15) G. W. Hollenberg, in Fabrication and Properties of Lithium Ceramics, Advances in Ceramics, Vol 25 G. W. Hollenberg and I. Hastings, Eds. (The American Ceramic Society, 1989) p. 186.

16) G. W. Hollenberg and D. L. Baldwin, J. Nucl. Mater. 133-134 (1985) 242.

17) F. Botter, B. Rasneur, and E. Roth, J. Nucl. Mater. (in press).

18) G. W. Hollenberg and D. L. Baldwin, J. Nucl. Mater. 133-134 (1985) 242.

19) J. L. Ethridge, D. E. Baker, and A. D. Miller, in Fabrication and Properties of Lithium Ceramics, Advances in Ceramics, Vol 25, G. W. Hollenberg and I. Hastings, Eds. (American Ceramic Society, Columbus, OH, 1989) p. 170.

20) C. E. Johnson and G. W. Hollenberg, J. Nucl. Mater. 122 & 123 (1984) 871.

21) H. Ohno, S. Konishi, T. Nagasahi, T. Kurasawa, H. Katsuta, and H. Watanabe, J. Nucl. Mater. 133 & 134 (1985) 181.

22) J. D. Fowley, R. A. Causey, D. Chandra, and T. S. Elleman, Proc. Inter. Conf., Gatlinburg, TN (1975).

23) R. Kitazawa and R. Coble, J. Amer. Cer. Soc. 57 (1974) 250.

24) I. J. Hastings, Ed., Proc. Specialists' Workshop on Modeling Tritium Behavior in Fusion Blanket Ceramics, Chalk River, Canada, April 23-24, 1987.

25) C. E. Johnson, Ed., Proc. Specialists' Workshop on Modeling Tritium Behavior in Fusion Ceramic Blankets, Indianapolis, Indiana, April 27-28, 1989.

26) J. P. Kopasz, S. W. Tam, and C. E. Johnson, J. Nucl. Mater. 155-157 (1988) 500.

27) G. Zwicker and K. Jacobi, Surf. Sci. 131 (1983) 179.

28) D. B. Rosenblatt and G. J. Dienes, J. Catal. 4 (1965) 71.

29) H. L. Gruber, J. Phys. Chem. 66 (1962) 48.

30) A. K. Fischer and C. E. Johnson, Fusion Techn. 15 (1989) 1212.

31) R. A. Verral, J. M. Miller. S. R. Bowka, and C. E. Johnson, in Fabrication and Properties of Lithium Ceramics, Advances in Ceramics, in Ceramics, Vol. 25, G. W. Hollenberg and I. Hastings, Eds. (American Ceramic Society 1989) p.41.

32) J. P. Kopasz, S. W. Tam, and R. A. Verral, Fusion Techn. 15 (1989) 1217.