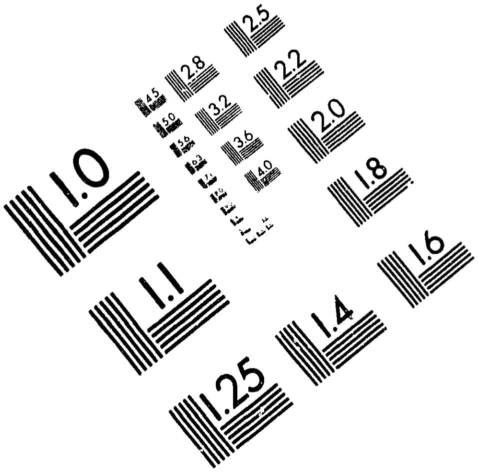
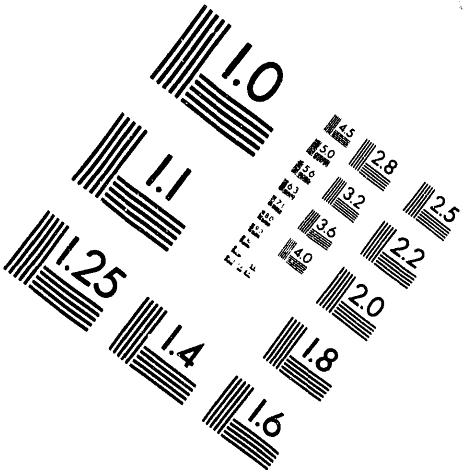
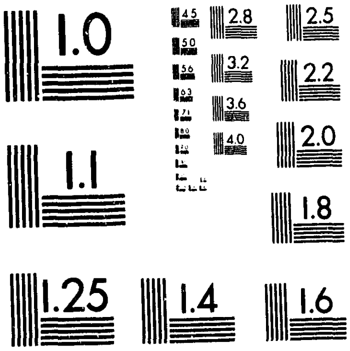


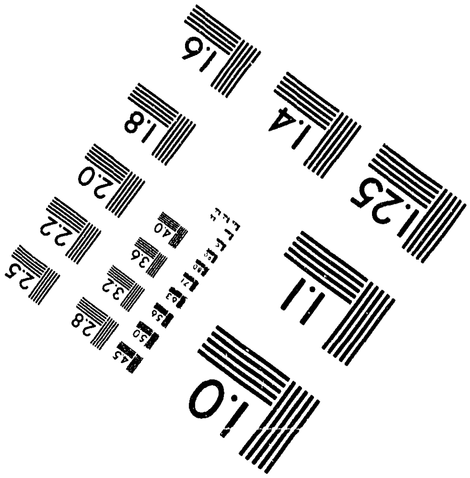
AIIM

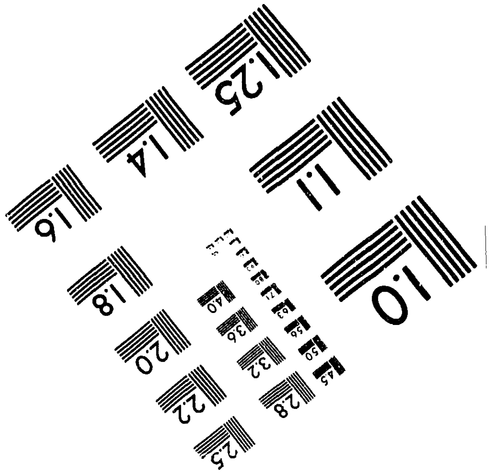
Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202









MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

Conf-9210255--2

Tritium Diffusion and Desorption in Single Crystal $LiAlO_2$

J. P. Kopasz, C. A. Seils, C. E. Johnson

Argonne National Laboratory
Chemical Technology Division

9700 S. Cass Ave
Argonne, IL 60439
USA

For International Workshop on Ceramic Breeder Blanket Interactions
Tokyo, Japan
October 1992

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

RECEIVED
JUN 14 1993
OSTI

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Introduction:

Tritium transport in lithium ceramics has received considerable attention because of their potential use as tritium breeding materials for fusion reactors. In particular, tritium transport in lithium aluminate has been investigated by several authors.[1-7] However, the mechanism of tritium transport and release from $LiAlO_2$ and the rate constants for diffusion in, and desorption from, $LiAlO_2$ are still uncertain. Tritium diffusivity values ranging over six orders of magnitude have been reported. In addition, the question as to whether diffusion or desorption is the rate-limiting mechanism is still being debated.

One of the possible reasons for the wide range in reported values for tritium diffusion is that some of them were determined under conditions where desorption was actually the rate-controlling mechanism. The method for determining the diffusion and desorption rate constants has generally been to observe the tritium release from the lithium ceramic and analyze the time dependence of the release process. The data are usually analyzed based on a diffusion, desorption, or a mixed diffusion-desorption model. However, complementary measurements that would indicate whether release is in the diffusion- or desorption-controlled regime are usually not made. Recently, Quanci[8] and Verrall[9] have employed mathematical tests based on the initial slopes of plots of the natural log of the fraction released versus time to determine whether release falls in the diffusion or desorption regime. However, the initial release behavior often does not follow the prescribed mathematics due to time delays in the experimental apparatus.

It may be possible to overcome these difficulties simply by examining the tritium distribution within the solid. In the bulk, contributions from desorption are expected to be small and should be limited to the near-surface region. The concentration gradient in the interior should, therefore, be less sensitive to the desorption rate constant, making it possible to obtain good values for the diffusion coefficients, even in the mixed diffusion-desorption regime.

Another possible contributing factor for the spread observed in the reported diffusivities is the presence of impurities in the ceramic materials. Impurities can alter the diffusivity by creating vacancies, interstitials, or other defects. In lithium aluminate, it has been postulated that tritium diffusion occurs via a lithium-vacancy tritium complex.[10] If this is the case, then impurities that affect the number of lithium vacancies should also affect the tritium diffusivity. The sensitivity of the tritium diffusivity to these impurities depends on the number of lithium vacancies caused by the impurity relative to those defects present in the pure material.

In an attempt to determine the diffusivity of tritium in lithium aluminate, we have performed isothermal anneal tests on single crystal samples (approximately 1.5 mm dia.). Large single crystals were used to minimize the contributions from desorption. Diffusion kinetics become more dominant as the crystal radius increases due to the decreasing surface area to volume ratio. However, the release may still be in the mixed diffusion-desorption regime which would make obtaining the rate constants from the time dependence of the tritium release difficult. Therfore, we have decided to section the samples and determine the diffusivity from the tritium concentration profile within the sample. In addition, in an attempt to understand the effects of impurities on the tritium transport, we have studied the tritium profiles in pure and Mg doped (0.3%) $LiAlO_2$.

Experimental

Single crystals of pure and Mg-doped $LiAlO_2$ were supplied by the Commisariat a L'Energie Atomic (CEA). The crystals were grown using the Czochralski technique, and the

Mg dopant level was determined to be 0.3% by spark source spectrometry.[11] The samples were dried under vacuum at 800°C for 4 hours and then packaged in aluminum capsules, which were cold-welded shut in an inert helim atmosphere glovebox. The capsules were irradiated in the Cadmium Lined Neutron Activation Tube at the University of Illinois, Urbana-Champaign, for 3 hours at a power level of 1500 kW. The cadmium lined facility was employed to harden the neutron spectrum and ensure that the tritium production within the single crystal was spatially uniform. The calculated amount of tritium produced is approximately 1 µCi per single crystal.

The single crystals were transferred from the aluminum capsules to a sample holder in an inert atmosphere glovebox. The sample holder was designed with two compression fittings, which enabled isolation of the sample from the atmosphere while it was being transferred from the glovebox to the annealing apparatus. The annealing apparatus was preheated to the desired temperature(500-800°C), and a purge flow established. The sample was then introduced to the furnace and annealed for a specified time. The released tritium was reduced in a zinc bed, detected with a proportional counter, oxidized over a CuO bed, and then trapped in ethylene glycol. After the anneal, the sample was 'quenched' by sliding it out of the furnace into a cool zone in the apparatus, causing a drop in sample temperature of 200°C in about 3-5 minutes. Cooling continued until the sample reached room temperature.

The tritium profile was measured by stepwise dissolution of the sample using the following procedure. After cooling, the sample diameter was measured three times with a spring-loaded dial micrometer. The sample was then placed in a vial containing 1 ml of an HCl/HF acid solution (6 N HCl, 0.5 N HF), which was placed in a thermostated bath at 50°C. After approximately 30 minutes in the bath, the vial was removed and 2 ml of water added. A 1ml aliquot of this solution was removed and placed in a scintillation vial along with 18 ml of scintillation cocktail. The remaining solution was pipetted out of the vial and discarded. The vial and crystal were washed four times with 1 ml of water. The crystal was then removed from the vial and blotted dry, and its diameter was measured three times with a dial micrometer. The crystal was then placed in a vial with 1 ml of acid solution, and the above steps repeated until the crystal size was too small to handle. At that point the crystal was left in the acid solution overnight, then 2 ml of water was added to the acid solution, and a 1 ml aliquot taken for scintillation counting. From these measurements, tritium profiles within the crystals were obtained.

Calculations

Tritium release from single-crystal lithium aluminate can be modeled using diffusion in the bulk with desorption occurring at the surface. The differential equations governing the tritium transport are:

$$\frac{\partial C}{\partial t}=D\left(\frac{\partial^2 C}{\partial r^2}+\frac{2}{r}\frac{\partial C}{\partial r}\right) \qquad (1)$$

for $0 \leq r < a$, and

$$\frac{\partial C}{\partial r}+\frac{K}{D}C=0 \qquad (2)$$

for $r=a$.

The solution to these equations for the case of a constant initial concentration C_i is given by[12]

$$C=\frac{2hC_i}{r}\sum e^{(-D\alpha_n^2 t)}\frac{a^2\alpha_n^2+(ah-1)^2}{\alpha_n^2[a^2\alpha_n^2+ah(ah-1)]}\sin(a\alpha_n)\sin(r\alpha_n) \tag{3}$$

Where C = concentration at position r
K = desorption rate constant
D=Diffusivity
h = K/D
C_i = initial concentration
a = crystal radius
r = radial position
t = time
α_n = roots of $a\alpha_n \cot(a\alpha_n)=1 - ah$

Although one can determine the diffusivity and desorption rate constant given the tritium concentration at the surface, the tritium concentration at the center, and the initial tritium concentration, we found a better method was to fit the total observed tritium profile to Eq. 3. This approach would minimize errors due to attempting to measure the very small crystals left near the end of the dissolution. Diffusivities were obtained by using the initial concentration and a minimization routine that fit the concentration data to Eq. 3.

Results and Conclusions

Representative plots showing the observed tritium profile and the fit to the data with the calculated diffusivity and desorption rate constant are shown in Figures 1- 2 for pure samples and in Figures 3-4 for Mg-doped samples. Results for the pure and Mg doped $LiAlO_2$ are tabulated in Figure 5. The diffusivity was observed to follow a simple Arrhenius-type temperature dependence, with the diffusivities determined for the doped and undoped materials being the same within experimental error. The calculated diffusivity is given by $\ln D = -2.246 - 1.519\times10^4/T$, yielding an activation energy of 30.1 kcal/mol.

The diffusivity determined in these samples is higher than most of the reported values. However, it is comparable to the values given by Botter,[3] and Bruning et al.,[1] which are several orders of magnitude above the other literature values. The desorption rate constants determined by this sectioning method exhibit some scatter. The scatter may be due to experimental difficulties in determining the concentration at the surface, or due to more complex surface desorption processes with different mechanisms contributing at different temperatures. The data from the Mg doped material suggests that there may be two desorption activation energies. This would be in agreement with previous TPD experiments which indicate several desorption mechanisms;[7] however, more data are needed.

Using the values determined for D and K in these large single crystals, and the rule that desorption will be rate controlling when the ratio aK/D is less than or equal to one (a = grain radius), we determined that for grain radii less than 100 µm, the tritium transport will be in the desorption controlled regime (see Fig. 6). Thus, for in-pile tests where a<100 µm these results suggest tritium release should be desorption controlled.

Acknowledgments

We would like to acknowledge Dr. N. Roux of Centre d'Etudes de Saclay, CEA, France for supplying us with single crystals of pure and Mg doped $LiAlO_2$. This work was supported by the United States Department of Energy, Office of Fusion Energy.

References

1) D. Bruning, D. Guggi, H. R. Ihle, Fusion Technology, 1982, 1, 543.
2) R. Clemmer et al. The TRIO Experiment, ANL-84-55, Argonne National Laboratory, September, 1984.
3) F. Botter, Proceedings of the 14th SOFT, September 1986, Avignon, France (Pergammon Press, New York) p. 1023.
4) K. Okuno and H. Kudo J. Nucl. Mater. 1986, 138, 357.
5) T. Kuraswa, H. Watanabe, G. W. Hollenberg, Y. Ishii, A, Nishimura, H. Yoshida, Y. Naruse, M. Aizawa, H. Ohno, and S. Konishi, J. Nucl. Mater. 1986, 141-143, 265.
6) S. Tanaka, A. Kawamoto,M. Yamawaki, T. Terai, Y. Takahashi, H. Kawamura, M. Saito Fusion Eng. and Des. 1989, 8,155 .
7) J.P. Kopasz, C. A. Seils, C. E. Johnson, J. Nucl.Mater. 1992, 191-194 ,231.
8) J. F. Quanci, Princeton University Dissertation, Department of Chemical Engineering,1989.
9) R. Verrall, Proceedings of the International Workshop on Ceramic Breeder Blanket Interactions, Novemver 22-23, 1991, Clearwater, Fl. p. 91.
10) J. P. Kopasz, S. W. Tam, C. E. Johnson, J. Nucl. Mater. 1991,179-181,816.
11) N. Roux, CEA, personal communication,1990.
12) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids", Clarendon Press, 1959.

Fig. 1

Observed and Calculated Tritium Profile
for Pure $LiAlO_2$ Annealed at 783°C for 4500 s
$(D=3.24\times10^{-8}\ cm^2/s,\ \ K=9.0\times10^{-6}\ cm/s)$

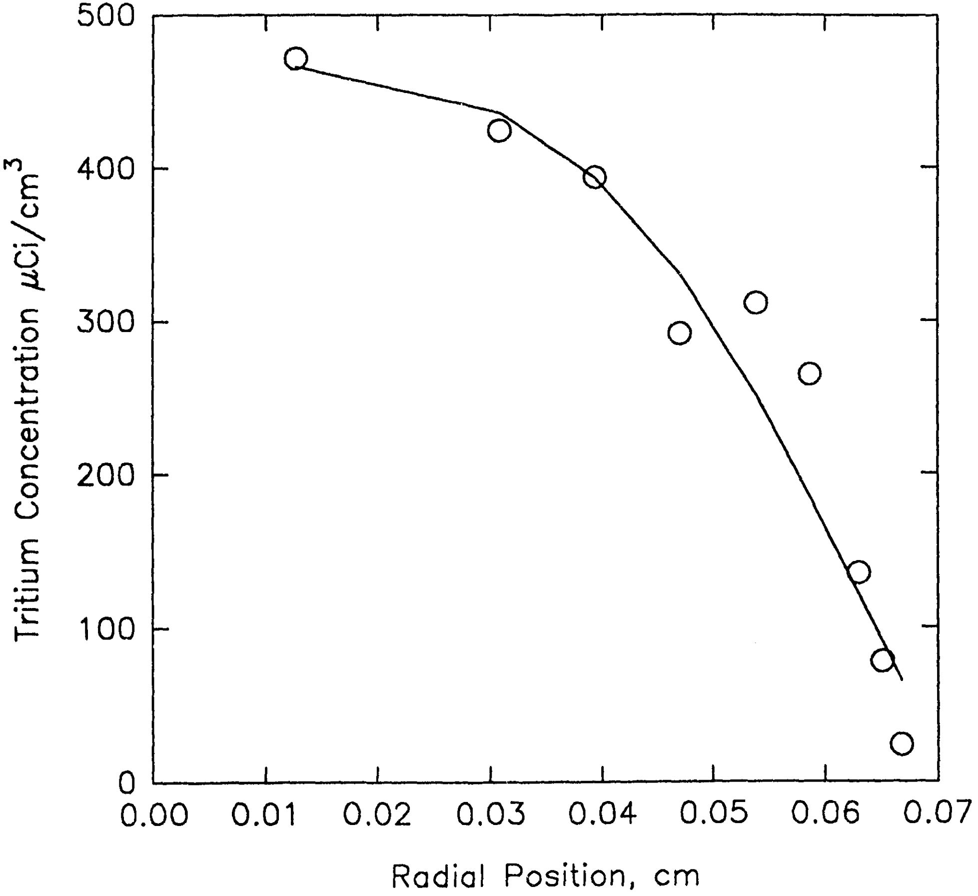


Fig. 2

Observed and Calculated Tritium Profile
for Pure $LiAlO_2$ Annealed at 606°C for 64500 s
($D=6.39\times10^{-9}\,cm^2/s$, $K=1.37\times10^{-7}\,cm/s$)

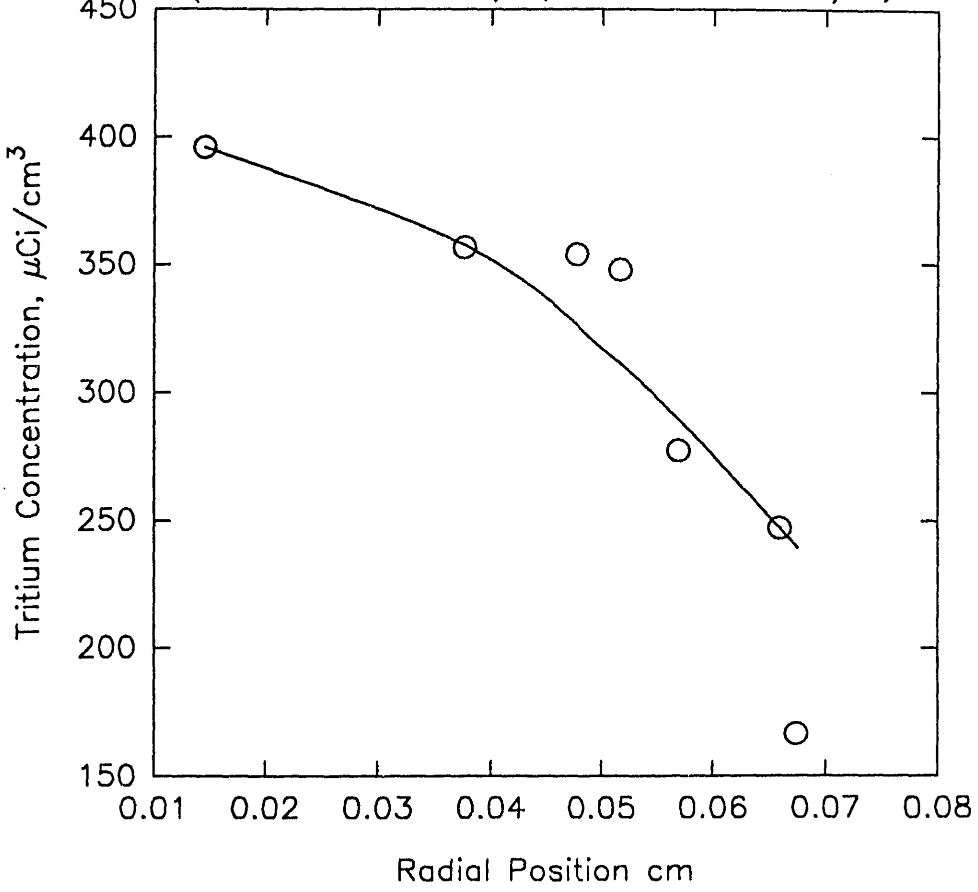
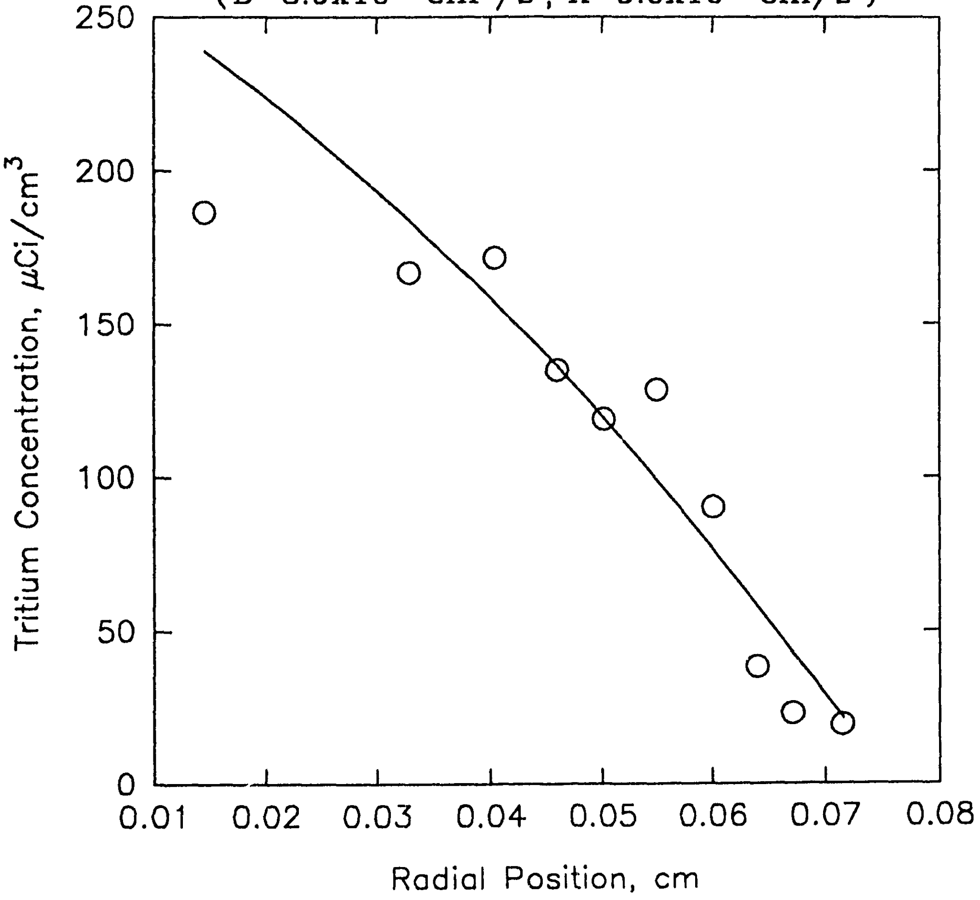
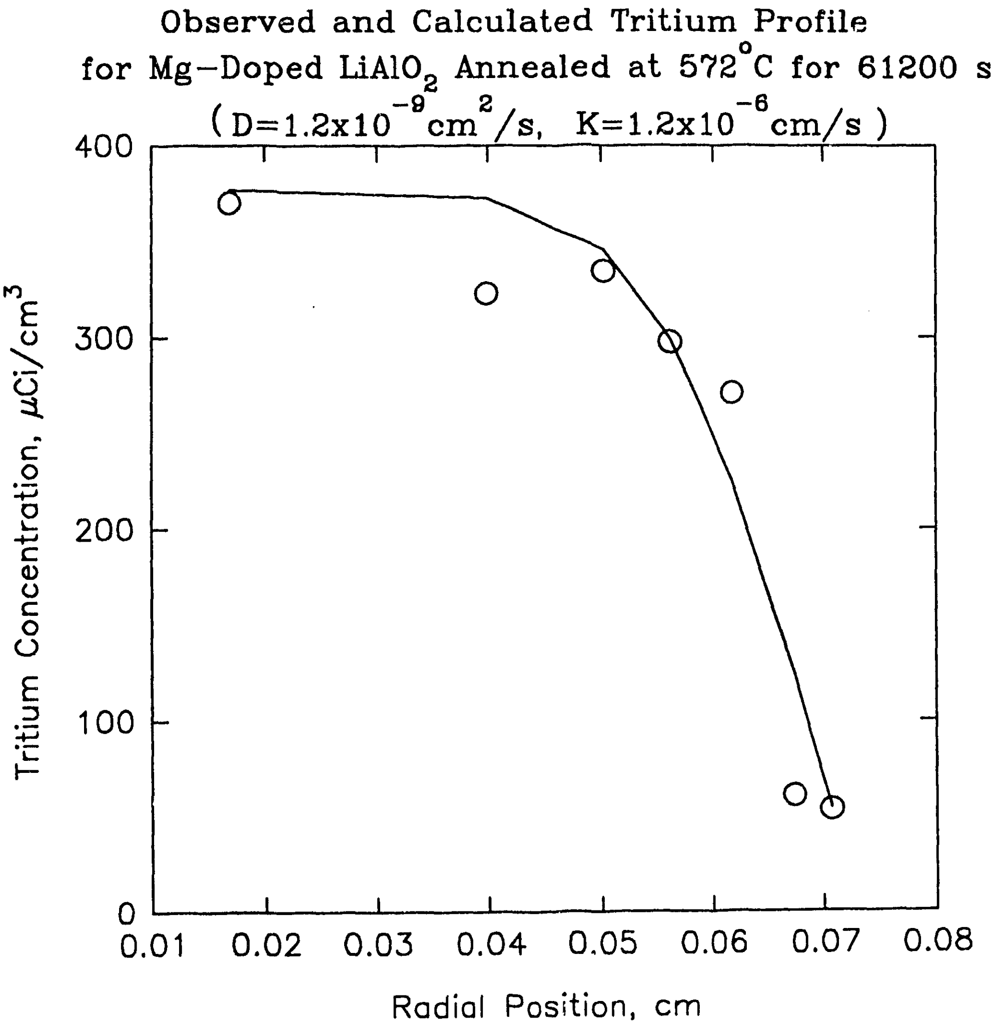


Fig. 3



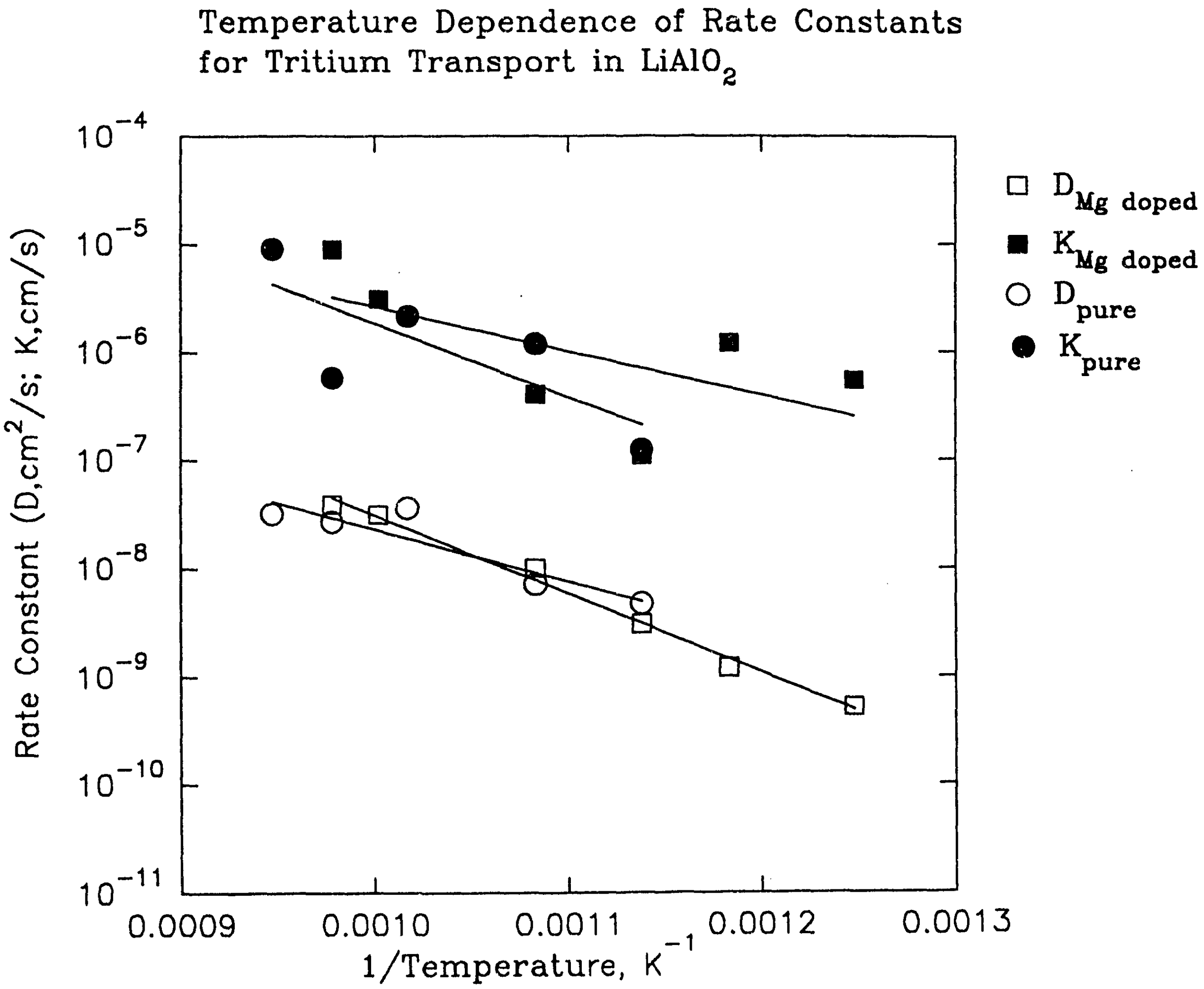
Observed and Calculated Tritium Profile
for Mg–Doped $LiAlO_2$ Annealed at 750°C for 18000 s
($D=3.9\times10^{-8}\ cm^2/s$, $K=9.0\times10^{-6}\ cm/s$)

Fig. 4



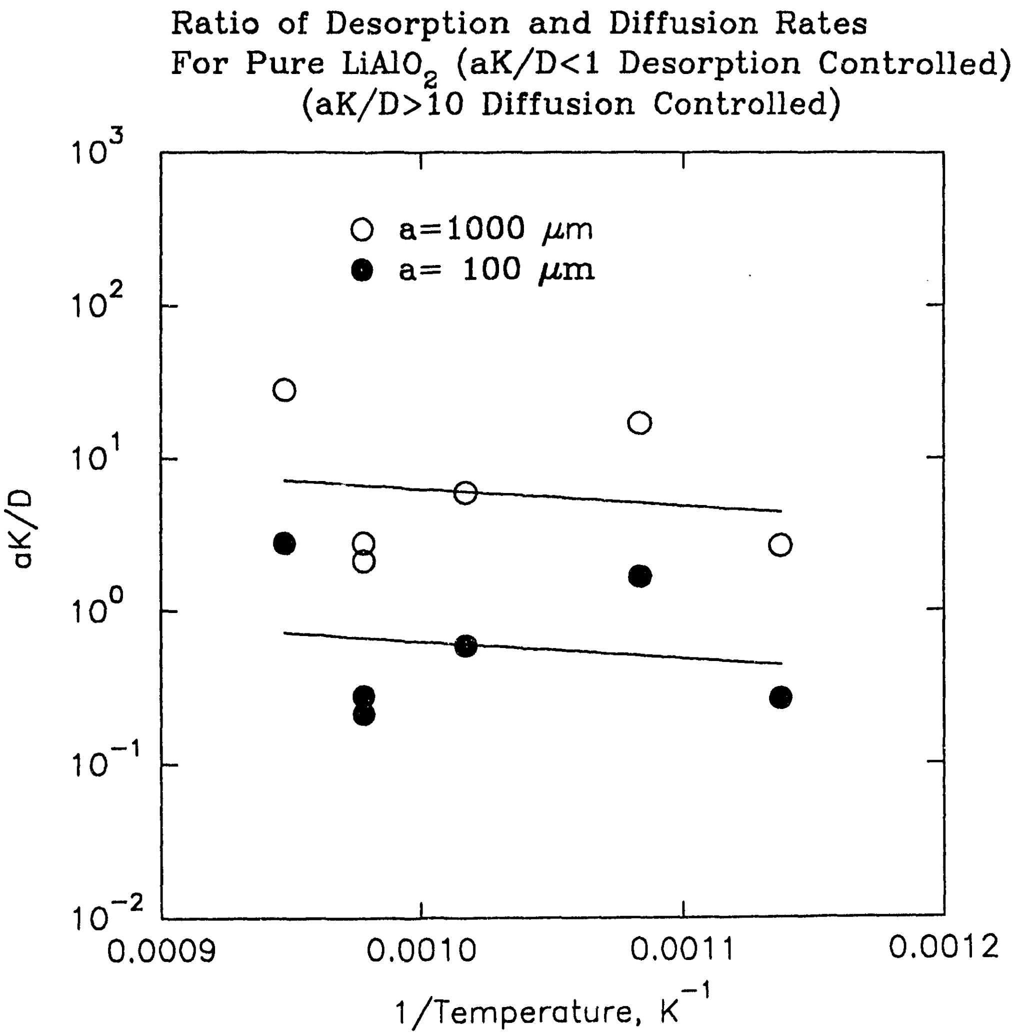
Observed and Calculated Tritium Profile
for Mg–Doped $LiAlO_2$ Annealed at 572°C for 61200 s
($D=1.2\times10^{-9}\ cm^2/s$, $K=1.2\times10^{-6}\ cm/s$)

Fig. 5



Temperature Dependence of Rate Constants for Tritium Transport in $LiAlO_2$

Fig. 6


Ratio of Desorption and Diffusion Rates
For Pure LiAlO$_2$ (aK/D<1 Desorption Controlled)
(aK/D>10 Diffusion Controlled)
○ a=1000 μm
● a= 100 μm
aK/D
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
0.0009
0.0010
0.0011
0.0012
1/Temperature, K^{-1}

DATE
FILMED

8/18/93

END