SOLID OXIDE COMPOUNDS - PROPERTIES NECESSARY
FOR FUSION APPLICATIONS*

by

P. A. Finn
Chemical Engineering Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL   60439

and

T. Kurasawa, S. Nasu, K. Noda, T. Takahashi,
H. Takeshita, T. Tanifuji, and H. Watanabe
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun
Ibaraki-ken, Japan 319-11

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Summary

An experimental program was conducted in collaboration with the staff at the Japan Atomic Energy Research Institute for the purpose of generating fusion pertinent thermophysical and chemical data on two ternary lithium oxides that have potential as tritium breeder materials, Li_2ZrO_3 and Li_2TiO_3. The four areas studied were: (1) fabrication, (2) thermal diffusivity/thermal conductivity, (3) compatibility with candidate structural alloys (HT-9, 316 SS, and Ni-plated 316 SS), and (4) tritium release behavior after irradiation. Where possible, the behavior of these materials was compared with lithium oxide.

Thermal conductivity was studied as a function of temperature and porosity--both ternary oxides had relatively low thermal conductivities (≤ 2 W/mK). In the compatibility tests done as a function of time and temperature, the oxides had the following relative reactivity for each alloy examined: $Li_2O > Li_2ZrO_3 > Li_2TiO_3$. Tritium release behavior was studied using the constant heating rate method. The effect of fluence, heating rate, flow gas, and impurities on the magnitude and temperature dependence of tritium release was determined.

Introduction

The establishment of breeder blanket technology is essential for the development of successful D-T fusion. Because the data base for candidate breeding materials is limited, experimental studies are required before their performance as breeding blankets can be accurately assessed. A preliminary study was conducted with Li_2ZrO_3 and Li_2TiO_3 to determine some properties important in fusion breeder blanket operation. The four areas studied were: fabrication, thermal diffusivity; compatibility between each ceramic and selected alloys (HT-9, 316 SS, Ni plated 316 SS); and tritium

release behavior after irradiation. These studies were done as a part of the U.S.-Japan Fusion Exchange Program.

Materials Characterization/Fabrication

Both Li_2ZrO_3 and Li_2TiO_3 were obtained from a commercial vendor (Alfa Products, Danvers, Massachusetts) and analyzed using X-ray diffraction, differential thermal/thermogravimetric analysis, and X-ray fluorescence. After heat treatment at 973 K for 4 h in vacuum to remove the volatile impurities, the Li_2ZrO_3 contained 1-2% each of Li_4ZrO_4 and ZrO_2. The Li_2TiO_3 after similar heat treatment contained 1-3% each TiO_2 (brookite), Li_4TiO_4, "$Li_2Ti_2O_5$" (previously unidentified and assumed isostructural with $Li_2Ti_3O_5$), and $LiTi_2O_4$. The small amount of hafnium (parts per million) in the Li_2ZrO_3 was not considered significant.

The dependence of the theoretical density (TD) and the associated open and closed porosity on pressure and sintering temperature was determined in order to reproducibly fabricate pellets ~12 mm in diameter and ~6 mm high with both materials. For Li_2ZrO_3 the pressed need to define density increased from 60 to 68% TD when the pressure was increased from 0.1 to 0.5 GPa. Heat treatment at 1173 K for 4 h in vacuum did not increase the TD. Scanning electron micrographs of the above material showed that the grains were 5-20 μm in size with connected pores each >5 μm. As the sintering temperature was increased from 1273 to 1573 K, the density increased from 64 to 88% of TD. A dependence on pressure was noted at sintering temperatures <1573 K. The grains in the 88% TD material were 20-80 μm in size with connected pores ≥15 μm; some glassiness in the material was noted. For all Li_2ZrO_3 pellets, the closed porosity was 4%; the open porosity ranged from 8-32%. The Li_2TiO_3 was cold pressed at 0.4 GPa. Heat treatment for 4 h in vacuum at 1373, 1573, or 1693 K produced pellets which were 70-72% TD, 74-76% TD, or 79-81% TD,

respectively. The grain size in 71% TD material was 40 μm with 10 μm connected pores; in the 81% TD pellet, grains were 110 μm in size with connected pores each >50 μm. As the density increased, the material appeared to become more glassy. For all samples, the closed porosity was 2%.

Thus, for both Li_2ZrO_3 and Li_2TiO_3, samples consisted of large grained material with low closed porosity and large open pore channels. The presence of closed pores may impede tritium release; therefore open pore channels are desirable. For Li_2O,[1] the open porosity has been found to decrease drastically at densities >86% of TD.

Thermal Diffusivity/Thermal Conductivity

For thermal-hydraulic analysis of fusion blankets, the thermal conductivity of the blanket materials as a function of temperature and porosity has to be known. The thermal conductivities of Li_2ZrO_3 and Li_2TiO_3 were determined using literature values for the heat capacity[2,3] and employing the laser pulse method to measure the thermal diffusivity, α. Measurements were made in vacuum as a function of temperature and porosity. The apparatus has previously been described[1]; its accuracy was verified by determining the thermal diffusivity of iron. For Li_2ZrO_3 and Li_2TiO_3, samples 10-11 mm in diameter and 0.7-1.0 mm thick were coated with carbon to ensure uniform absorption of the laser pulse energy and heated at 1073 K in vacuum to remove water and other adsorbed materials. The input heat pulse was 0.7 ms; the half time for the back surface temperature rise was ≥ 200 ms.

For Li_2ZrO_3, the measured thermal diffusivity was low. It increased from 0.001 cm^2/s at 400 K to ~0.005 cm^2/s at ≥ 1300 K for samples preheated at 1073 K. (For samples preheated to lower temperatures, the thermal diffusivity decreased between 400 and 700 K and then increased.) When the temperature was cycled during a thermal diffusivity experiment, hysteresis was noted. For Li_2TiO_3 the thermal diffusivity ranged between 0.004 and 0.006 cm^2/s, but two types of behavior were noted in the dependence of diffusivity on temperature and porosity. The classical thermal diffusivity curve was noted for samples which had been prepared by sintering at 1373 K; for those sintered above 1373 K (where no gross grain growth was observed), the thermal diffusivity first decreased and then increased starting at ~800 K, producing an S-shaped curve.

The magnitude of the thermal diffusivity of Li_2ZrO_3 compares with that measured for ZrO_2[4] (0.006 cm^2/s). An increase in thermal diffusivity is noted with stabilized ZrO_2,[5] but the origin of this effect was not elucidated. It may be due to ionic or electronic contributions which would become significant at relatively low temperature because the thermal diffusivity is so low. For two titanate systems,[6,7] it was found that microcracking could increase or decrease the thermal diffusivity as a function of temperature and simultaneously generate hysteresis effects. A theoretical paper,[8] which has pertinence to these experimental results, notes that both the presence and the amount of a glass phase can change the shape of the diffusivity curve and also lower the magnitude. For both Li_2ZrO_3 and Li_2TiO_3, these results have significant impact since both materials appeared glassy and were composed of large grains, which enhances cracking effects. Thus, one might expect deviation from the classical thermal diffusivity curve. The measurements may also have been affected by the presence of non-stoichiometric material. The diffusivity in another system,[9] where the stoichiometry was varied, was lowered non-uniformly as a function of temperature and stoichiometry. One last experimental observation should be noted. It has been found[10] that for materials with low diffusivity, the presence of a gas (e.g., helium, argon) can increase the diffusivity by 50%. For the ternary oxides which will be used with helium, this would have a significant impact on the thermal-hydraulic analysis of a given breeder blanket design.

For both Li_2ZrO_3 and Li_2TiO_3, the heat capacity is a smoothly increasing function. Therefore, the shapes of the thermal conductivity curves are similar to those obtained for thermal diffusivity. For Li_2ZrO_3, the thermal conductivity increased from ~0.3 to ~2 W/mK; for Li_2TiO_3, it ranged between 1.5-2.2 W/mK. The thermal conductivities of these two materials as well as for other solid lithium oxides[1,11] are generally low compared to other oxides.

In Fig. 1, the thermal conductivities of some lithium oxides are shown as a function of temperature. The position of any of these curves could be shifted or their shapes could be modified by changes in any of the following factors: grain size, pore structure, presence of a glass phase, microcracking, non-stoichiometry, non-vacuum conditions, impurities. Therefore, these curves only serve as a guide for choosing the best blanket material on the basis of thermal-hydraulic performance

in the expected operating temperature range for a solid oxide blanket (700-1100 K). However, parametric analysis[12] tend to indicate that reducing the thermal conductivity from 3 to 1 W/mK may not severely impact the blanket thermal hydraulics and the associated breeding ratio. Instead, the primary criteria for material selection will probably be the characteristics which control tritium release, i.e., grain size and pore structure.
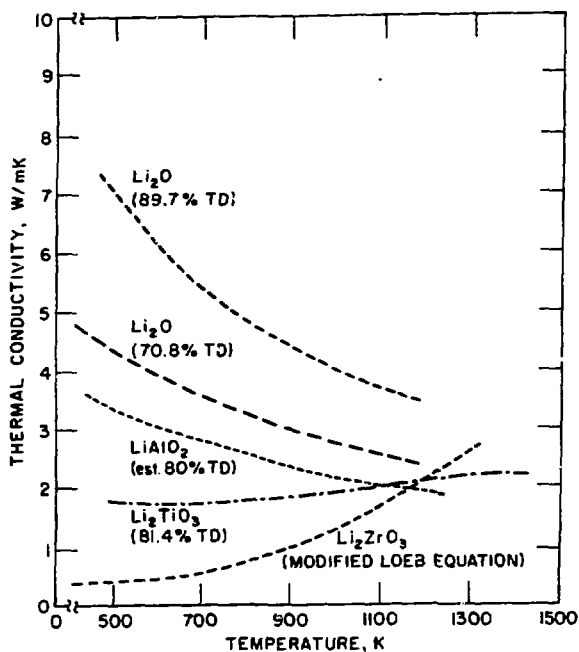

Fig. 1. Thermal conductivity of selected ceramic breeder compounds as a function of temperature.

Compatibility

Blanket modules are expected to remain structurally stable for extended periods (1-6 y). Therefore, the effect of long-term contact of a given oxide with a given alloy must be evaluated. Accelerated tests, i.e., those run at high temperature for short times, have been utilized to scope the behavior of a given combination in a given environment.

In this study, compatibility tests were conducted on oxide/alloy couples composed of 75% TD Li_2TiO_3, 88% TD Li_2ZrO_3 or 86% TD Li_2O[13] with HT-9, 316 SS, or Ni-coated 316 SS (20 μm). Each ceramic was in a separate experimental assembly with couples stacked under light tension.[14] The assemblies were held at 923 K for 410 h or at 823 K for 1035 h in ~10^5 Pa helium (static).

After completion of the test, samples were weighed, penetration depth was measured, and x-ray diffraction was used to determine the products formed. The results (Fig. 2) showed appreciable formation of scale for the couples Li_2O/HT-9, Li_2O/316 SS, and Li_2ZrO_3/HT-9; the other couples formed minor amounts of scale. A summary (Table 1) of the species present showed that for couples where large amounts of scale were formed, an iron compound was the major constituent, whereas $LiCrO_2$ was the major surface constituent if minor amounts of scale were formed. The formation of $LiCrO_2$ may have inhibited further reaction. Li_5FeO_4 was present on the Li_2O surfaces in contact with HT-9 and 316 SS. No new species were found on Li_2ZrO_3 or Li_2TiO_3, but both the ZrO_2 and TiO_2 content had increased.
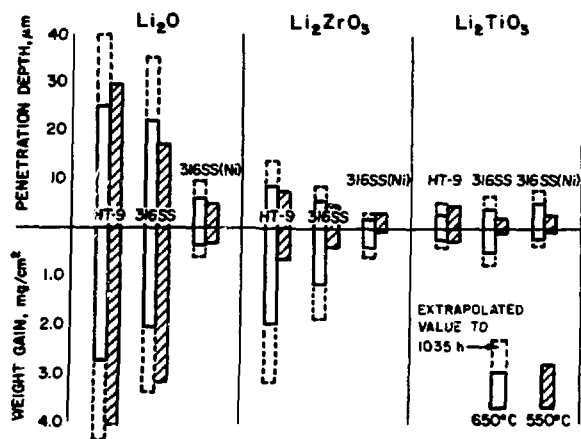

Fig. 2. Summary of results obtained in compatibility tests with Li_2O, Li_2ZrO_3 and Li_2TiO_3.

Reaction Products on Alloys[a]

Ceramic	Li_2O		Li_2ZrO_3		Li_2TiO_3	
Alloy	Major	Minor	Major	Minor	Major	Minor
HT-9	Li_5FeO_4.	$LiCrO_2$	$LiFeO_2$,[b]	$LiCrO_2$	$LiCrO_2$.	$LiFeO_2$[b]
316 SS	Li_5FeO_4.	$LiCrO_2$	$LiFeO_2$,[b]	$LiCrO_2$	$LiCrO_2$.	$LiFeO_2$[b]
316 SS (Ni Plating)	$LiCrO_2$	-	$LiCrO_2$.	$LiFeO_2$[b]	$LiCrO_2$.	$LiFeO_2$[b]

[a]Identification from X-ray and corroborated from XMA.
[b]β and γ forms.

Reaction Products on Ceramics

Li_5FeO_4	- Li_2O surface (not plated)
ZrO_2	- increased
TiO_2	- increased

Table 1. Summary of Reaction Products Formed During Compatibility Tests

For all couples tested, iron and chromium diffused to the surface, forming $LiCrO_2$ and iron compounds (Li_5FeO_4 or $LiFeO_2$). The couples may not be useable for long-term fusion reactor operation.

Tritium Release

In a breeder blanket module, one of the main goals is to breed and then recover the tritium formed. A means whereby the tritium release characteristics can be simply evaluated is out-of-pile heat treatment tests.[15] In this study, 88% TD Li_2ZrO_3 and 76% TD Li_2TiO_3 were irradiated at 10^{15}, 10^{16}, and 10^{17} n/cm^2. After 30-60 d, the tritium release was measured at a constant heating rate (10 K/min or 1 K/min) and sweep gas flow rate (100 mL/min) using helium or hydrogen. With both materials, the major species detected was HTO but significant amounts of HT may have been present. (Experimental configuration precluded the resolution of this issue.)

For Li_2ZrO_3, there were two release peaks ($\sim$equal size) located at 695 K and 770 K for a sample irradiated at 10^{17} n/cm^2 and heated at 1 K/min hydrogen. The peak locations were shifted to higher temperature when (1) a faster heating rate was used, (2) helium was used, or (3) the samples were exposed to air/moisutre. The peaks were shifted to lower temperature when the samples were irradiated at lower fluences. The change in release behavior after exposure to air is shown in Fig. 3.

For Li_2TiO_3, two release peaks were observed; the one at higher temperature was smaller. The maxima for samples irradiated at 10^{17} n/cm^2 were at 634 K and 743 K at 1 K/min in hydrogen. The peaks were shifted to higher temperature when faster heating rates were used or when helium was used. Exposure to air/moisture, resulted in a tailing effect toward higher temperature. The peaks were not appreciably shifted with increasing fluence but the shapes did change.

The Li_2ZrO_3 and Li_2TiO_3 samples were dissolved in HF after being heated to 1173 K in the above experiments to determine the residual tritium. Since Li_2ZrO_3 samples contained a γ-contaminant, only an upper limit on tritium content was obtained (<0.02 wppm). For Li_2TiO_3, the tritium residue was 0.0003 wppm.

The tritium release behavior of Li_2ZrO_3 and Li_2TiO_3 is compared to that of lithium oxide[15] in Fig. 4. The figure is intended to be of qualitative not quantitative significance because: (1) many factors (grain size,
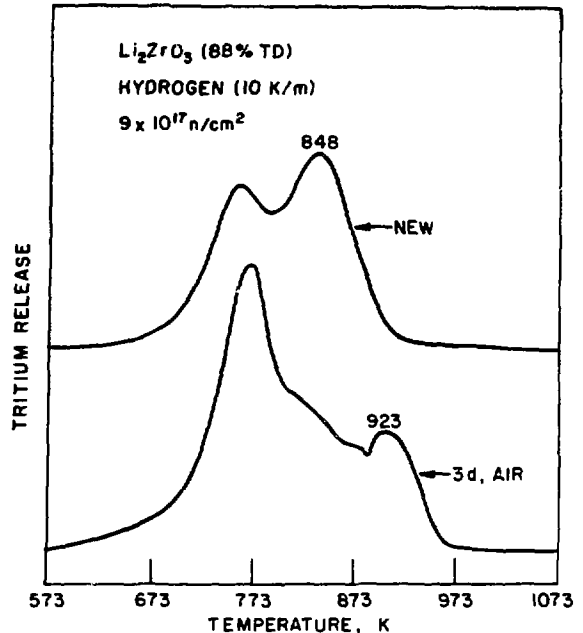

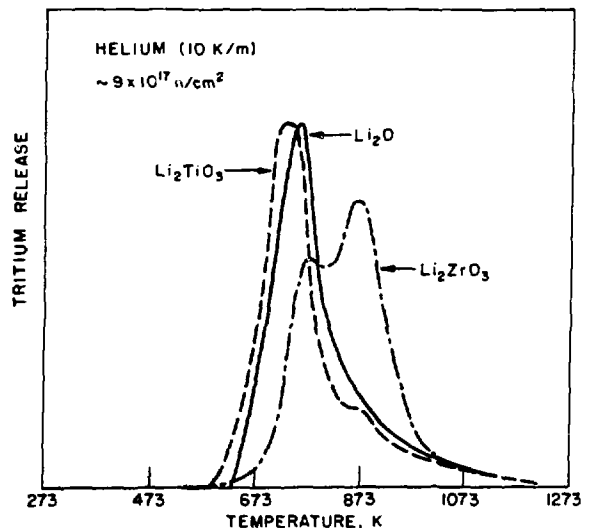Fig. 3. Tritium release behavior of neutron-irradiated Li_2ZrO_3.

Fig. 4. Tritium release behavior of neutron-irradiated Li_2O (86% TD), Li_2ZrO_3 (88% TD), and Li_2TiO_3 (76% TD) for similar conditions.

temperature, moisture) affect the tritium release characteristics, both out-of-pile and in situ, (2) out-of-pile results do not necessarily represent in situ tritium release behavior and (3) radiation effects at 10^{22} n/cm^2 (fusion levels) may be quite different than those measured at $\leq 10^{17}$ n/cm^2. Nonetheless, it can be seen that the tritium release behavior of Li_2TiO_3 is quite

similar to Li_2O's, whereas, for Li_2ZrO_3 higher temperatures ($\sim100°$) are required. The behavior of $LiAlO_2$ could probably resemble that of Li_2ZrO_3.

Conclusions

- The fabrication of sintered pellets of Li_2ZrO_3 and Li_2TiO_3 resulted in samples with large grain sizes and large connected pores.

- Both Li_2ZrO_3 and Li_2TiO_3 have low thermal conductivities (≤2 W/mK) relative to other oxides.

- Li_2TiO_3 was found to be compatible with all alloys tested whereas Li_2ZrO_3 formed appreciable scale with HT-9 as did Li_2O with both HT-9 and 316 SS. The formation of $LiCrO_2$ at the interface may hinder scale formation. Nickel plating (~20 μm) on 316 SS reduced the formation of scale with Li_2O.

At slow heating rates in hydrogen Li_2TiO_3 released most tritium below 740 K whereas Li_2ZrO_3 released most tritium below 820 K. The Li_2TiO_3 release behavior was similar to Li_2O's.

Acknowledgment

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