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LITHIUM-BASED OXIDE CERAMICS FOR TRITIUM-BREEDING APPLICATIONS

MCDONNELL DOUGLAS ASTRONAUTICS COMPANY-ST. LOUIS DIVISION

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JUNE 1983

Prepared by D. J. SUITER

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ABSTRACT

Material preparation techniques, crystallographic data, phase diagrams, metal compatibility, and thermal properties have been assembled for the lithium-based oxide ceramics designated as potential solid tritium breeders for fusion devices. The materials discussed in this report include: Li_2O , $\beta\text{-Li}_5\text{AlO}_4$, $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , Li_2SiO_3 , Li_4TiO_4 , Li_2TiO_3 , Li_8ZrO_6 , Li_4ZrO_4 , and Li_2ZrO_3 . The thermal properties covered were vaporization, thermal conductivity, specific heat, and linear thermal expansion.

There has been no attempt to rank the above mentioned candidates, but rather to merely indicate points that must be considered when using the various materials as solid breeders. These encompass low lithium-atom densities, destructive phase transformations, a higher thermal expansion, low thermal conductivity, excessive vaporization at low temperatures, corrosive nature toward metals, and difficulty in sample preparation.

TABLE OF CONTENTS

	PAGE
TITLE PAGE	i
ABSTRACT	ii
LIST OF FIGURES	vi
SUMMARY	ix
1.0 INTRODUCTION	1-1
1.1 REFERENCES	1-2
2.0 PREPARATION OF LITHIUM BASED OXIDE CERAMICS	2-1
2.1 INTRODUCTION	2-1
2.2 Li-O SYSTEM	2-1
2.3 Li ₂ O-Al ₂ O ₃ SYSTEM	2-3
2.3.1 Li ₅ AlO ₄	2-3
2.3.2 LiAlO ₂	2-4
2.4 Li ₂ O-SiO ₂ SYSTEM	2-6
2.4.1 Li ₄ SiO ₄	2-6
2.4.2 Li ₂ SiO ₃	2-7
2.5 Li ₂ O-TiO ₂ SYSTEM	2-8
2.5.1 Li ₄ TiO ₄	2-8
2.5.2 Li ₂ TiO ₃	2-8
2.6 Li ₂ O-ZrO ₂ SYSTEM	2-9
2.6.1 Li ₈ ZrO ₆	2-9
2.6.2 Li ₄ ZrO ₄	2-10
2.6.3 Li ₂ ZrO ₃	2-10
2.7 REFERENCES	2-11
3.0 CRYSTALLINE PROPERTIES	3-1
3.1 INTRODUCTION	3-1
3.2 Li-O SYSTEM	3-1
3.3 Li ₂ O-Al ₂ O ₃ SYSTEM	3-6
3.4 Li ₂ O-SiO ₂ SYSTEM	3-14
3.5 Li ₂ O-TiO ₂ SYSTEM	3-21
3.6 Li ₂ O-ZrO ₂ SYSTEM	3-26
3.7 REFERENCES	3-34

TABLE OF CONTENTS (CONT'D.)

	PAGE
4.0 THERMAL PROPERTIES	4-1
4.1 INTRODUCTION	4-1
4.2 MELTING POINTS	4-2
4.3 VAPORIZATION	4-2
4.3.1 Li_2O	4-2
4.3.2 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM	4-6
4.3.3 $\text{Li}_2\text{O}-\text{SiO}_2$ SYSTEM	4-10
4.3.4 $\text{Li}_2\text{O}-\text{TiO}_2$ SYSTEM	4-12
4.3.5 $\text{Li}_2\text{O}-\text{ZrO}_2$ SYSTEM	4-12
4.3.6 Li_2O - METAL OXIDE SYSTEMS	4-13
4.4 THERMAL CONDUCTIVITY	4-15
4.4.1 Li_2O	4-15
4.4.2 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM	4-17
4.4.3 $\text{Li}_2\text{O}-\text{SiO}_2$ SYSTEM	4-17
4.4.4 $\text{Li}_2\text{O}-\text{TiO}_2$ SYSTEM	4-19
4.4.5 $\text{Li}_2\text{O}-\text{ZrO}_2$ SYSTEM	4-19
4.4.6 Li_2O - METAL OXIDE SYSTEMS	4-21
4.5 SPECIFIC HEAT	4-22
4.5.1 Li_2O	4-22
4.5.2 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM	4-22
4.5.3 $\text{Li}_2\text{O}-\text{SiO}_2$ SYSTEM	4-23
4.5.4 $\text{Li}_2\text{O}-\text{TiO}_2$ SYSTEM	4-25
4.5.5 $\text{Li}_2\text{O}-\text{ZrO}_2$ SYSTEM	4-26
4.6 THERMAL EXPANSION	4-27
4.6.1 Li_2O	4-27
4.6.2 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM	4-28
4.6.3 $\text{Li}_2\text{O}-\text{SiO}_2$ SYSTEM	4-30
4.6.4 $\text{Li}_2\text{O}-\text{TiO}_2$ SYSTEM	4-32
4.6.5 $\text{Li}_2\text{O}-\text{ZrO}_2$ SYSTEM	4-32
4.6.6 Li_2O - METAL OXIDE SYSTEMS	4-33
4.7 MISCELLANEOUS	4-34
4.7.1 Li_2O	4-34
4.7.2 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM	4-35

TABLE OF CONTENTS (CONT'D.)

PAGE

4.7.2.1 β - Li_5AlO_4	4-35
4.7.2.2 γ - LiAlO_2	4-35
4.7.2.3 LiAl_5O_8	4-35
4.7.3 $\text{Li}_2\text{O-SiO}_2$ SYSTEM	4-36
4.7.3.1 Li_4SiO_4	4-36
4.7.3.2 Li_2SiO_3	4-36
4.7.3.3 $\text{Li}_2\text{Si}_2\text{O}_5$	4-36
4.7.4 $\text{Li}_2\text{O-TiO}_2$ SYSTEM	4-37
4.7.5 $\text{Li}_2\text{O-ZrO}_2$ SYSTEM	4-38
4.7.5.1 Li_8ZrO_6	4-38
4.7.5.2 Li_4ZrO_4	4-38
4.7.5.3 Li_2ZrO_3	4-38
4.8 REFERENCES	4-39
5.0 COMPATIBILITY OF LITHIUM CERAMICS AND METALS	5-1
5.1 INTRODUCTION	5-1
5.2 Li-O SYSTEM	5-1
5.3 $\text{Li}_2\text{O-Al}_2\text{O}_3$ SYSTEM	5-12
5.4 $\text{Li}_2\text{O-SiO}_2$ SYSTEM	5-12
5.5 $\text{Li}_2\text{O-TiO}_2$ SYSTEM	5-12
5.6 $\text{Li}_2\text{O-ZrO}_2$ SYSTEM	5-12
5.7 REFERENCES	5-13

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
3.2.1	PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{CO}_3\text{-Li}_2\text{O}$ ACCORDING TO PAPIN, ET AL.	3-2
3.2.2	PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{CO}_3\text{-Li}_2\text{O}$ ACCORDING TO SMIRNOV, ET AL.	3-3
3.2.3	PROJECTED PHASE DIAGRAM OF THE SYSTEM $\text{LiOH-Li}_2\text{O}$. . .	3-4
3.2.4	CRYSTALLOGRAPHIC DATA FOR LITHIUM OXIDE	3-5
3.3.1	PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{O-Al}_2\text{O}_3$	3-6
3.3.2	CRYSTALLOGRAPHIC DATA FOR LITHIUM META-ALUMINATE . . .	3-8
3.3.3	CRYSTALLOGRAPHIC DATA FOR TETRAOXO-LITHIUM-ALUMINATE .	3-12
3.4.1	PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{O-SiO}_2$	3-15
3.4.2	CRYSTALLOGRAPHIC DATA FOR LITHIUM ORTHOSILICATE . . .	3-17
3.4.3	CRYSTALLOGRAPHIC DATA FOR LITHIUM METASILICATE	3-19
3.5.1	PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{O-TiO}_2$	3-22
3.5.2	CRYSTALLOGRAPHIC DATA FOR LITHIUM ORTHOTITANATE . . .	3-23
3.5.3	CRYSTALLOGRAPHIC DATA FOR LITHIUM METATITANATE	3-25
3.6.1	CRYSTALLOGRAPHIC DATA FOR OCTALITHIUM ZIRCONATE . . .	3-27
3.6.2	CRYSTALLOGRAPHIC DATA FOR LITHIUM ORTHOZIRCONATE . . .	3-30
3.6.3	CRYSTALLOGRAPHIC DATA FOR LITHIUM METAZIRCONATE . . .	3-32
4.2.1	MELTING POINTS OF SOLID BREEDER CANDIDATES	4-3
4.3.1.1	Li PARTIAL PRESSURE OVER Li_2O IN A Pt KNUDSEN CELL . .	4-4
4.3.1.2	VARIOUS PARTIAL PRESSURES OVER Li_2O IN A Pt KNUDSEN CELL	4-4
4.3.1.3	Li_2O PARTIAL PRESSURE OVER Li_2O IN A Pt KNUDSEN CELL .	4-5
4.3.1.4	Li PARTIAL PRESSURE OVER Li_2O IN KNUDSEN CELLS OF VARIOUS METALS	4-6
4.3.2.1	Li PARTIAL PRESSURE OVER $\beta\text{-Li}_5\text{AlO}_4$ (s,l) IN A Pt KNUDSEN CELL	4-7

LIST OF FIGURES (CONT'D.)

FIGURE NO.	TITLE	PAGE
4.3.2.2	VARIOUS PARTIAL PRESSURES OVER γ -LiAlO ₂ IN A Pt KUNDSSEN CELL	4-8
4.3.2.3	Li PARTIAL PRESSURES OVER γ -LiAlO ₂ IN A Pt KUNDSSEN CELL	4-9
4.3.2.4	Li PARTIAL PRESSURES OVER γ -LiAlO ₂ IN KNUDSEN CELLS OF VARIOUS METALS	4-9
4.3.2.5	PARTIAL PRESSURES OVER LiAl ₅ O ₈ IN A Pt KNUDSEN CELL	4-10
4.3.3.1	PARTIAL PRESSURES OVER Li ₂ SiO ₃ IN A Pt KNUDSEN CELL	4-11
4.3.5.1	Li PARTIAL PRESSURE OVER THE Li ₂ O-ZrO ₂ SYSTEM IN Pt KNUDSEN CELLS	4-12
4.3.6.1	Li PARTIAL PRESSURE OVER SOLID BREEDER CANDIDATES IN Pt KNUDSEN CELLS	4-14
4.3.6.2	Li PARTIAL PRESSURE OVER CORROSION PRODUCTS FOUND DURING Li ₂ O/METAL COMPATIBILITY EXPERIMENTS	4-14
4.4.1.1	THERMAL CONDUCTIVITY OF CRYSTALLINE Li ₂ O	4-16
4.4.2.1	THERMAL CONDUCTIVITY OF CRYSTALLINE LiAlO ₂	4-18
4.4.3.1	THERMAL CONDUCTIVITY OF CRYSTALLINE Li ₄ SiO ₄	4-18
4.4.4.1	THERMAL CONDUCTIVITY OF CRYSTALLINE Li ₂ TiO ₃	4-20
4.4.5.1	THERMAL CONDUCTIVITY OF CRYSTALLINE Li ₂ ZrO ₃	4-20
4.4.6.1	COMPARISON OF THERMAL CONDUCTIVITY VALUES FOR VARIOUS SOLID BREEDER CANDIDATES	4-21
4.5.1.1	SPECIFIC HEAT OF Li ₂ O	4-23
4.5.2.1	SPECIFIC HEAT OF γ -LiAlO ₂	4-24
4.5.3.1	SPECIFIC HEAT OF COMPOUNDS IN THE Li ₂ O-SiO ₂ SYSTEM	4-25
4.5.4.1	SPECIFIC HEAT OF Li ₂ TiO ₃	4-26
4.5.5.1	SPECIFIC HEAT OF Li ₂ ZrO ₃	4-27

LIST OF FIGURES (CONT'D.)

FIGURE NO.	TITLE	PAGE
4.6.1.1	LINEAR THERMAL EXPANSION OF SINGLE CRYSTAL AND CRYSTALLINE Li_2O	4-28
4.6.2.1	LINEAR THERMAL EXPANSION OF CRYSTALLINE $\gamma\text{-LiAlO}_2$ AND LiAl_5O_8	4-29
4.6.3.1	LINEAR THERMAL EXPANSION OF COMPOUNDS IN THE $\text{Li}_2\text{O-SiO}_2$ SYSTEM	4-31
4.6.4.1	LINEAR THERMAL EXPANSION OF CRYSTALLINE Li_2TiO_3 . . .	4-32
4.6.5.1	LINEAR THERMAL EXPANSION OF CRYSTALLINE Li_2ZrO_3 . . .	4-33
4.6.6.1	COMPARISON OF LINEAR THERMAL EXPANSION OF SOLID BREEDER CANDIDATES	4-34
5.2.1	LITHIA/METAL COMPATIBILITY RESULTS	5-2
5.2.2	RATE OF OXIDE SCALE FORMATION ON METAL/ Li_2O REACTION COUPLES IN A 10^{-5} TORR ENVIRONMENT	5-9
5.2.3	RATE OF OXIDE SCALE FORMATION ON METAL/ Li_2O REACTION COUPLES IN A STATIC He ENVIRONMENT	5-10
5.2.4	CHEMICAL COMPOSITIONS OF METAL REACTION COUPLE SPECIMENS	5-11

SUMMARY

The physical preparation of the candidate powders has not proven to be an insurmountable task in as much as the majority can be made using simple solid state reaction techniques. Li_2O has presented the most problems from a powder preparation standpoint with its tendency to absorb CO_2 and H_2O , its volatility and reactivity with container materials at high temperatures. For Li_2O , as well as the others, great care has to be taken to achieve relatively small batches of high purity, single phase powders. In addition, these lithium based oxides have displayed a strong tendency to absorb chlorine compounds from the air, containers, or even in a controlled atmosphere glove box. This presents further difficulties in powder production, storage, and specimen fabrication to insure low levels of Cl, to prevent stress corrosion during irradiation. Test sample fabrication with all materials has been accomplished once good quality powders were obtained. If, for example, test pellets were required to possess a final $\approx 1 \mu\text{m}$ grain (crystallite) size or high density, then hot pressing has been the solution with little or no surface contamination. If the grain size or density requirement were removed, then all of the powders can be cold pressed and sintered, still paying special regard to: 1) the P_{O_2} of the sintering atmosphere to retard Li volatilization, 2) the "dryness" of the sintering atmosphere so as to minimize (if not eliminate) CO_2 and H_2O absorption, and 3) the interaction of the solid breeder with its setter plate during sintering. Cold pressing and firing to high densities has been difficult due to the lack of work on the use of additives to retard grain growth.

With the exception of the $\text{Li}_2\text{O}-\text{ZrO}_2$ system, at least partial phase diagrams exist for the remaining candidate material systems. Such diagrams are essential in predicting the results of any deviations from stoichiometry such as might occur during irradiation with Li burnup. In addition, any crystallographic transformations must be noted and investigated to determine whether or not they are destructive transformations and if they lie in the temperature range of solid breeder operation. This information can be invaluable in assessing solid breeders as shown by Dr. Hollenberg's work illustrating that the phase transformation in Li_4SiO_4 , previously thought to be destructive thus reducing its chances from a solid breeder consideration, was only displacive in nature and solid pellets or rods would hold together and not crack as the transformation temperature was surpassed. Very little crystallographic

information exists for the compounds Li_8ZrO_6 and Li_4ZrO_4 and almost none concerning the relationships (solid solution's, etc.) that are found within the Li_2O - ZrO_2 system.

Some thermal property data have been generated for the majority of solid breeders. As a leading candidate, Li_2O has received the most attention with extensive work being done on specific heat, vaporization rates and products, effect of porosity on thermal conductivity and on linear expansion coefficients. The others, with the exception of Li_8ZrO_6 and Li_4ZrO_4 , have received some interest for basic property data. While thermal conductivity measurements exist for the remaining ones with the exception of Li_8ZrO_6 and Li_4ZrO_4 , they do not address the porosity dependence, effect of grain size or the effects of atmospheric conditions on the thermal conductivity. This kind of data will be needed to help predict the solid breeder's thermal performance in actual operation. Vaporization rates for Li_4SiO_4 have not been generated and the effect of moisture in the atmosphere during vaporization has only been "seen" in Li_2O . Thermal conductivity, specific heat, and thermal expansion values are non-existent for Li_8ZrO_6 and Li_4ZrO_4 and are needed to properly evaluate these materials.

Most of the metal compatibility experiments have centered on Li_2O because it is regarded as the most corrosive of all the materials. Nickel and nickel-based alloys performed the best, regardless of environment or which solid breeder material was used. Data for the majority of remaining candidates are limited or do not exist. Some of the studies have postulated that the Li_2O itself is not the problem but that of LiOH , and that if the LiOH concentration can be minimized or eliminated, then Li_2O compatibility problem will be substantially reduced.

This report has dwelt on available data for nonirradiated specimens, but as these materials are assessed the effects of irradiation (tritium release, dimensional changes, phase transformations, nonstoichiometry, etc.) will need to be taken into account.

1.0 INTRODUCTION

Fusion power reactors that utilize the D-T fuel cycle will be required to breed and recover tritium in quantities at least equal to its composition. The most cost-effective approach involves the transmutation of lithium atoms by neutrons to form helium and the needed tritium. Debate has centered on whether the utilized form of the lithium should be a liquid metal, liquid salt, metal alloy, or oxide-based ceramic. The leading candidates appear to be liquid lithium or a lithium alloy, which have the advantage of being both a tritium breeder and a coolant in the first wall blanket. However, the liquid metals are highly flammable and corrosive and present serious safety concerns if leaks develop. The solid lithium-based oxide ceramics are being investigated as an alternate to the liquid metals.

A number of blanket and shield design studies⁽¹⁻⁴⁾ that investigated the use of solid breeders have identified Li_2O , $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , Li_2SiO_3 , Li_2TiO_3 , and Li_2ZrO_3 as candidate materials having the capability of achieving the desired net breeding ratios within the first wall blanket. Currently Li_2O , which is considered the leading solid breeding oxide since it has a Li atom fraction greater than liquid Li and does not require a neutron multiplier to increase the tritium breeding ratio (TBR) to ≥ 1 . Other compounds that are also of interest fall within the following four systems: $\text{Li}_2\text{O-Al}_2\text{O}_3$, $\text{Li}_2\text{O-SiO}_2$, $\text{Li}_2\text{O-TiO}_2$, and $\text{Li}_2\text{O-ZrO}_2$.

In order to make valid decisions on these compounds, material property data must be available. The focus of this effort is to begin a centralized data base that will concentrate on material preparation techniques, crystallographic data, phase diagrams, thermal conductivity, specific heat, thermal expansion, and metal compatibility. Also necessary for comparisons would be tritium diffusion coefficients but while there has been an abundance of tritium diffusion data from irradiation experiments involving the lithium-based oxide ceramics, meaningful interpretations have been difficult to derive. Okula and Sze⁽⁵⁾ reviewed the bulk of the irradiation experiments involving solid breeders through 1979 and reported widely scattered data at low temperatures and low fluence conditions. At present, irradiation experiments are underway or being planned that will produce more definitive results at

the higher, more blanket-like operating temperatures and fluences. As a result of the uncertainties that exist in the present, available tritium diffusion data for solid breeders, it will not be covered in this report.

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2.0 PREPARATION OF LITHIUM BASED COMPONENTS

2.1 INTRODUCTION

Since the selected solid breeder material must not only meet phase purity requirements but also grain (or crystallite) size and impurity limitations, it is important to know what previous avenues have been followed and their results. Attempts/successes at producing the Li-based oxides, by methods in the laboratory are discussed below.

2.2 Li-O SYSTEM

2.2.1 Li_2O

Lithium oxide (Li_2O) can be usually obtained by following any of four reactions:

Pierron⁽¹⁾ reported dissolving lithium metal (Li) in liquid ammonia and then injecting oxygen into the blue solution until it turned clear. The solution was then evaporated to dryness, leaving a residue of lithium peroxide (Li_2O_2) and Li_2O . Subsequent heating to 300°C for several hours decomposed the peroxide, leaving an Li_2O sample. No purity data were given for the sample.

Equations (3) and (4) are the more conventional routes taken to produce Li_2O , and they can be performed in air, vacuum, or inert atmosphere with varying degrees of success. Van Arkel et al.⁽²⁾ decomposed lithium hydroxide (LiOH) in a platinum (Pt) container @ 1000°C for several hours in vacuum, and then initiated melting point determination for Li_2O . No impurities were listed

and no interaction with the Pt crucible was reported. The Joint Committee on Powder Diffraction Standards (JCPDS) card #12-254 stated that the Li_2O used to produce the indexed pattern had been derived by decomposing LiOH @ 650°C in a Ag boat in an inert environment protected from atmospheric CO_2 and H_2O . The final product contained 0.1-1.0 wt.% calcium (Ca), 0.01-0.1 wt.% sodium (Na), 0.001-0.01 wt.% aluminum (Al), silicon (Si), and vanadium (V), but no particle size was reported.

Brewer and Margrave⁽³⁾ used the thermal decomposition of lithium carbonate (Li_2CO_3) to produce the Li_2O for their melting point experiments. They decomposed the carbonate in a Pt crucible under high vacuum by gradually heating to 1000°C and pumping off the CO_2 . The reaction was complete in 1-4 hours, and when their product was analyzed by x-ray fluorescence, no Pt impurity was detected.

Arons et al.⁽⁴⁾ found that slow heating of Li_2CO_3 under a vacuum (10^{-3} torr) invited unwanted Pt contamination in high purity samples. Instead, he quickly heated the Li_2CO_3 in a Pt crucible by induction heating. By this technique the sample temperature reached 1200 - 1300°C in 5-10 minutes and the process was completed within 30 minutes. The Pt crucible used was not cleaned between batches but allowed to develop a reaction layer which inhibited the transfer of Pt to the sample to less than 10 wppm. By employing this technique, Arons et al. were able to minimize the Total Metallic Impurities (TMI) to < 200 wppm and LiOH to < 0.5 wt.%. The crystallite size of the Li_2O was initially in the 10 - $30 \mu\text{m}$ region but could be reduced to $< 10 \mu\text{m}$ by ball milling for 8-24 hours under a dry inert gas environment. High-density Al_2O_3 grinding media and a jar mill were used to limit impurity pick-up due to ball milling to < 100 wppm TMI, predominately Al_2O_3 and SiO_2 .

Larsen and Ortman⁽⁵⁾ have recently developed a processing approach to Li_2O where LiOH is converted to Li_2O_2 in a nitrogen atmosphere glove box slowly heated under a 10^{-3} torr vacuum in a pyrex tube to 297°C , and then heated in a Pt crucible to 800°C for 2-10 days. The final product had only 0.03 wt.% Pt and 0-0.2 wt.% LiOH and Li_2CO_3 . Larsen and Ortman contend that slow heating is the key for removing Li_2CO_3 and LiOH , which are considered to be more reactive with Pt than Li_2O . They used their material for melting point determinations and in reactions with other oxides.

Anno and Boeing ⁽⁶⁾ employed a patented two-stage process to produce porous Li_2O slugs and microspheres. In the first stage, under an argon atmosphere, anhydrous LiOH was melted @ 500°C in an Ag crucible and then cooled to room temperature. Next, the solidified LiOH sample was heated to $150^\circ - 200^\circ\text{C}$ and then to 700°C under 10^{-5} torr to insure decomposition of LiOH to Li_2O . The result was a 98.1 wt.% pure Li_2O slug with an average pore spacing of $\approx 5 \mu\text{m}$. The remaining 1.9 wt.% was determined to be LiOH with no mention of any metallic impurities. The above method was modified to produce porous, $100 \mu\text{m}$, Li_2O microspheres with an average pore spacing $\leq 10 \mu\text{m}$. In this process, the molten LiOH was fed through a small bore vertical tube to form a liquid jet which was disrupted, with the resulting microspheres of LiOH being cooled under argon. The LiOH microspheres were then similarly converted to Li_2O microspheres as with the bulk samples.

Thornton et al. ⁽⁷⁾ were partially successful in making Li_2O microspheres by decomposing Li_2O_2 granules in a plasma. Due to a lack of a controlled atmosphere, the microsphere samples range in composition from 22 to 65 wt.% Li_2O with the remainder being LiOH . They indicated further work was needed to increase the Li_2O percentage to acceptable levels. No metallic impurities were reported for the Li_2O samples.

Shindo et al. ⁽⁸⁾ successfully developed a procedure for Li_2O single crystal production. Since Li_2O was so reactive with available crucible materials, they chose a floating zone technique whereby a feed rod and a seed rod were suspended at one of the foci of an infrared imaging furnace with 1.5 kw halogen lamp and ellipsoidal reflector to create the heat needed for melting. The furnace atmosphere consisted of a high purity argon gas to minimize CO_2 and H_2O pick-up.

2.3 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM

2.3.1 Li_5AlO_4

Guggi et al. ⁽⁹⁾ prepared $\alpha\text{-Li}_5\text{AlO}_4$ according to the reaction:

by heating a mixture (mole ratio, 5:1) of Li_2O_2 and $\alpha\text{-Al}_2\text{O}_3$ in a Ag boat to 500°C in dry air for 140 hours. The high temperature phase, $\beta\text{-Li}_5\text{AlO}_4$, was produced by either heating $\alpha\text{-Li}_5\text{AlO}_4$ in a Ag boat in an argon stream at 850°C for 72 hours or by calcining $\alpha\text{-Li}_5\text{AlO}_4$ to 1000°C in a Pt crucible under a high vacuum. No particle size or purity information were reported, in either approach.

Lehmann and Hesselbarth⁽¹⁰⁾ tempered a mixture of Li_2O and $\alpha\text{-Al}_2\text{O}_3$ at 500°C in air to produce $\alpha\text{-Li}_5\text{AlO}_4$. If Li_2CO_3 was used in place of the Li_2O , the reaction did not proceed to completion even at 600°C .

LaGinestra et.al.⁽¹¹⁾ used a $\gamma\text{-Al}_2\text{O}_3$, precipitated from $\text{Al}(\text{NO}_3)_3$ in an ammonia solution, as a raw material because of its higher surface area and thus its higher reactivity in the solid state. They were able to form $\gamma\text{-Li}_5\text{AlO}_4$ using both Li_2O_2 or Li_2O with $\gamma\text{-Al}_2\text{O}_3$. At temperatures below 500°C phases such as Li_2O and $\gamma\text{-Al}_2\text{O}_3$ were still present where as at higher temperatures ($600^\circ - 700^\circ\text{C}$) the phases of $\gamma\text{-LiAlO}_2$, LiO and $\gamma\text{-Li}_5\text{AlO}_4$ were observed. In addition, when Li_2CO_3 or LiNO_3 was used as a starting reagent, $\gamma\text{-LiAlO}_2$ was obtained, regardless of temperature. Crucible material, particle size, and purity were not revealed by the authors.

Hoppe and Konig⁽¹²⁾ used $\beta\text{-Li}_5\text{AlO}_4$ single crystals to refine the crystalline data for this material. The single crystals were produced by reacting Li_2O , obtained from LiOH decomposition, and Al_2O_3 in a Ni-lined, high pressure, calorimeter at 740°C for 14 days under an Ar atmosphere. Stewner and Hoppe⁽¹³⁾ made $\alpha\text{-Li}_5\text{AlO}_4$ single crystals in a similar manner but only heated to 700°C for 2 days in a Ni-lined, high-pressure calorimeter. No purity specifications for either crystal were discussed.

2.3.2 LiAlO_2

The preparation of lithium aluminate (LiAlO_2) in any of its three forms (α, β, γ) has centered around two reactions:

Hummel⁽¹⁴⁾ prepared γ -LiAlO₂ by ball milling Li₂CO₃ and Al₂O₃ in a distilled water slurry, drying and then calcining in Al₂O₃ crucibles @ 1300°C for 7 to 15 hours. No purity and particle size data were given.

Guggi et al.⁽⁹⁾ prepared γ -LiAlO₂ from a stoichiometric mixture of finely ground Li₂O and α -Al₂O₃ which was pressed into pellets and heated @ 900°C for 30 hours in a Pt boat in air. The pellets were then sealed in a Mo tube by electron beam welding, heated to 2000°C and cooled. The fused material contained $\approx$ 300 wppm Mo.

Lejus and Collongues⁽¹⁵⁾ mixed aluminum acetate (Al₃C₂H₃O₂) with the Li₂CO₃ and produced α -LiAlO₂ upon heating to 580°C. Lehmann and Hesselbarth⁽¹⁶⁾ fired an equimolar mixture of Li₂CO₃ and α -Al₂O₃ @ 600°C and got α -LiAlO₂. Marezio and Remeika⁽¹⁷⁾ subjected γ -LiAlO₂ to a pressure of 35 kbar @ 850°C and, after quenching to room temperature, found α -LiAlO₂. Although the sample was in a Ta container, no contamination was reported.

Chang and Margrave⁽¹⁸⁾ reported a high-pressure, high-temperature synthesis for β -LiAlO₂. They pressed a 2:1 molar mixture of Li₂O₂ and AlN @ 22 kbar @ 550° for 11 hours. When the time was lengthened to 25 hours, α -LiAlO₂ was formed. Tantalum served as the die lining, with little contamination reported.

Strickler and Roy⁽¹⁹⁾ produced α -LiAlO₂ by dissolving LiNO₃ and Al(NO₃)₃·9H₂O in deionized water, adding NH₄OH, and then evaporating the H₂O on a steam bath. Afterwards, the material was put into a Pt crucible and decomposed @ 750°C for several hours. This procedure resulted in a partly amorphous material which was converted to fully crystalline @ 950°C and above. No purity or particle size was reported.

Arons et al.⁽⁴⁾ ball milled high purity α -Al₂O₃, with a grain size of <0.02 μ m, and Li₂CO₃ in methanol. The slurry was then centrifuged, dried, and calcined in Al₂O₃ crucibles @ 650°C for 72-96 hours in air yielding a phase-pure α -LiAlO₂ with a particle size of $\approx$ 0.1 μ m. Another technique for α -LiAlO₂ production involved making a slurry of aqueous lithium acetate (LiC₂H₃O₂) and fine grained α -Al₂O₃, then spray drying before calcination. Agglomerates of the α -LiAlO₂ powder were cold pressed and fired in air to 1000°C-1100°C for

1 hour to convert α to γ -LiAlO₂. Firing at 1200°C in air resulted in γ -LiAlO₂ with a minor amount of LiAl₅O₈ due to partial Li₂O volatilization. Contamination of either powders was not mentioned.

Gurwell⁽²⁰⁾ analyzed one of the commercially available LiAlO₂ powders and discovered $\approx$ 3 wt.% unreacted Li₂CO₃ and both α and γ -LiAlO₂ phases. Particle sizes ranged from 150 to 30 μ m for the material.

Single crystals of γ -LiAlO₂ were grown from a flux as described by Marezio⁽²¹⁾. The flux, consisting of Li₂CO₃, α -Al₂O₃, B₂O₃ and PbO, was placed in a Pt crucible, heated to 1300°C for 5 hours, and then slowly cooled to room temperature. The γ -LiAlO₂ single crystals were extracted from the solidified flux by using acetic acid to remove the B₂O₃ and PbO compounds leaving only the γ -LiAlO₂ crystals. No purity data was offered by the author.

2.4 Li₂O-SiO₂ SYSTEM

2.4.1 Li₄SiO₄

Equation (8) has been used by many investigators to produce Li₄SiO₄ for their work.

Soga⁽²²⁾ prepared Li₄SiO₄ for thermal expansion measurements by wet milling Li₂CO₃ and SiO₂ under alcohol and heating the mixture in a Pt crucible at 1100°C for 20 hours. No mention was made of the material's chemical purity or of any reaction with the Pt crucible.

Dubey and West⁽²³⁾ reacted Li₂CO₃ and SiO₂ in Au foil boats @ 700°-800°C for 24 hours to produce Li₄SiO₄ in order to study its high-low crystallographic transformation. Hodge et al.⁽²⁴⁾ following a similar path as Dubey, reacted the mixture in Au foil boats @ 600°C to remove the bulk of the CO₂ and finally fired @ 800°-900°C for one to two days. Wittman and Modern⁽²⁵⁾ used a Pt crucible and heated the mixture to 1350°C to accomplish the reaction in several hours. Final product purities were not reported in these cases. Kracek⁽²⁶⁾

heated highly purified Li_2CO_3 and quartz (SiO_2) @ $750^\circ\text{--}800^\circ\text{C}$ to get Li_4SiO_4 in a Pt crucible, but noticed that the crucible had been severely attacked and was lined with an olive-gray deposit. Suiter⁽²⁷⁾ noticed similar olive-gray deposits on a Pt crucible after heating a mixture of high purity Li_2CO_3 and SiO_2 at 750°C for 2 days in flowing He. Although both powders had less than 5 wppm Pt initially, the final product contained ≈ 1000 wppm Pt.

Suiter et al.⁽²⁸⁾ prepared high purity (< 500 wppm TMI) Li_4SiO_4 by an organometallic route using Li_2CO_3 dissolved in acetic acid and tetraethylorthosilicate $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$, in isopropyl alcohol. The solutions were mixed, heated to dryness, and slowly calcined in SiO_2 crucibles @ $700^\circ\text{--}800^\circ\text{C}$ to produce the desired result. Reaction times took anywhere from 4-24 hours, depending upon the sample size. Particle sizes ranged from 30 to $10\text{ }\mu\text{m}$ and were easily reduced to $<5\text{ }\mu\text{m}$ by dry ball milling for 8-48 hours the powder in a high density Al_2O_3 jar with Al_2O_3 grinding medium under an inert gas atmosphere. The sample impurity level only increased ≈ 100 wppm Al due to the ball milling operation.

Tranqui et al.⁽²⁹⁾ grew Li_4SiO_4 single crystals from a $\text{LiOH}\cdot\text{H}_2\text{O}$ and SiO_2 melt @ 1250°C in a Pt crucible by the Czochralski pulling technique. Single crystals were obtained by polynucleation of the melt on a Pt wire and then pulling to small diameters to effect single crystal growth. Total impurities were listed at 0.5 wt.%, with no individual breakdown being reported.

2.4.2 Li_2SiO_3

The most common approach to Li_2SiO_3 has been:

Hess⁽³⁰⁾ melted the above reactants @ 1240°C to get Li_2SiO_3 , while West⁽³¹⁾ utilized the same raw materials but heated them to $600^\circ\text{--}700^\circ\text{C}$ and then to $800^\circ\text{--}850^\circ\text{C}$ for 24-48 hours. Neither investigator reported the crucible composition, the particle size nor the purity data of the finished powders.

Noshiro and Jitsurgiri⁽³²⁾ melted silicic acid ($\text{H}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$) and Li_2CO_3 @ 1400°C - 1500°C in a Pt crucible, in air, for 3-5 hours, and an amorphous Li_2SiO_3 was obtained. However, by subsequent heat treating @ 750°C for 24 hours, the Li_2SiO_3 was 100% crystallized. Lithium glasses require much greater SiO_2 contents (> 70 wt. %) in order to be stable in the temperature ranges of interest. Lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) for example, is used in some glass-ceramic systems and is partially crystallized in the 400 - 600°C temperature region. Bennington et al.⁽³³⁾ heated a stoichiometric mixture of reagent grade Li_2CO_3 and silicic acid in a Ni crucible for 8 days @ 700°C , 3 days @ 800°C and 4 days @ 900°C ; finally, the material was heated for 8 days @ 1100°C in Pt before being OK to determine the heat capacity of Li_2SiO_3 . Both groups of investigators did not discuss purity data or particle size distributions for their materials.

2.5 $\text{Li}_2\text{O}-\text{TiO}_2$ SYSTEM

2.5.1 Li_4TiO_4

Dubey and West^(23, 34) prepared Li_4TiO_4 by the reaction

The reactants were heated in air and contained in an Au boat. If the reaction was carried out for only a few hours, the product contained Li_4TiO_4 with small amounts of Li_2CO_3 and Li_2TiO_3 . Li_4TiO_4 was found to react readily with CO_2 and if left exposed to air for several weeks, a 50% conversion to Li_2CO_3 and disordered Li_2TiO_3 occurred. In addition, Li_4TiO_4 readily reacted with Pt at temperatures above 800°C , especially in the presence of CO_2 . No purity or particle size was listed for the products.

2.5.2 Li_2TiO_3

While equation (11) has been used extensively to produce Li_2TiO_3 , process parameters have differed.

Lokotosh and Lisnyak⁽³⁵⁾ were able to produce Li_2TiO_3 by calcining the reactants @ 900°C in air for 4 hours while King⁽³⁶⁾ needed 70 hours @ 1000°-1050°C in a Ni crucible and 30 hours @ 1150°C in a Pt crucible to achieve his goal. Impurities from King's procedure were listed as 0.03 wt. % Si and 0.06 wt. % Ni and Pt. In the work of Girard et al.⁽³⁷⁾, the reactants were fired @ 1250°C in air, ground in a porcelain ball mill for 4-5 hours in acetone, dried, pelletized and refired @ 1250°C to insure homogeneity.

Saikali⁽³⁸⁾ decomposed $\text{Li}_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ @ 600°C in air to give Li_2TiO_3 , while Morgan⁽³⁹⁾ successfully precipitated Li_2TiO_3 from a solution of titanium tetraisopropylate in isopropanol that had been blended into a cold concentrated lithium hydroxide solution and then brought to a boil. No particle size or purity information was revealed in either study.

2.6 $\text{Li}_2\text{O-ZrO}_2$ SYSTEM

2.6.1 Li_8ZrO_6

Neubert and Guggi⁽⁴⁰⁾ formed Li_8ZrO_6 by heating Li_2O and ZrO_2 in a Pt crucible according to:

The reaction was carried out in an argon stream to eliminate $\text{CO}_2/\text{H}_2\text{O}$ interaction with the Li_2O . Scholder et al.⁽⁴¹⁾ reacted Li_2O and ZrO_2 at 500°C for 12 hours and then to 550°C for 5 hours to get Li_8ZrO_6 . Belyaev and Annopol'skii⁽⁴²⁾ heated LiOH and ZrO_2 @ 950°C for 20 hours in air before they got a homogeneous product. At less times or temperatures, the reaction proceeded slowly and resulted in mixed phases, mainly Li_2ZrO_3 and Li_8ZrO_6 . In addition, when Li_2CO_3 was used as a starting material, the powders always contained mixed phases. Plyushchev and Grizik⁽⁴³⁾ used Li_2CO_3 and LiOH together with ZrO_2 in ratios up to 6:1 and still found Li_2ZrO_3 in the temperature range of 800°-1400°C.

Larsen and Ortman⁽⁵⁾ ground fused Li_2O and ZrO_2 under an inert gas atmosphere,

pressed a pellet, and fired it in a Pt boat in vacuum @ 590°C for 24 hours. The pellet was then cooled, reground and reheated for another 16 hours at 590°C to insure Li_8ZrO_6 homogeneity. In none of the aforementioned studies were particle size and purity information discussed.

2.6.2 Li_4ZrO_4

Neubert and Guggi⁽⁴⁰⁾ formed Li_4ZrO_4 in a Pt boat by

They found that if the raw materials were reacted at lower temperatures, the product was contaminated with significant amounts of Li_8ZrO_6 as well as unreacted ZrO_2 and Li_2ZrO_3 . It was also important that the starting mixture be quickly heated to avoid Li_8ZrO_6 information, due to slow thermal energy transfer. A small batch size also helped in reducing this possibility. Scholder et al.⁽⁴¹⁾ went to 1000°C for 3 hours to insure product phase purity.

Belyaev and Annopol'skii⁽⁴²⁾ produced Li_4ZrO_4 by heating LiOH and ZrO_2 @ 950°C for 20 hours in air. They found that the reaction of Li_2CO_3 and ZrO_2 at 550°-750°C for even 1 hour led to the formation of Li_2ZrO_3 , irrespective of the original reagent ratio.

2.6.3 Li_2ZrO_3

Several investigations^(35, 42, 44, 45) were able to produce Li_2ZrO_3 in a Pt boat in air by

Belyaev and Annopol'skii⁽⁴²⁾ found that the same reaction @ 550°C-750°C for 1 hour leads to the formation of Li_2ZrO_3 , irrespective of the original reagent ratio. In mixtures of LiOH and ZrO_2 , on the other hand, Li_2ZrO_3 was the only product formed between 350° and 580°C.

Dittrich and Hoppe⁽⁴⁶⁾ heated Li_2O and ZrO_2 in an O_2 atmosphere for 7 hours @ 900°C and then 30 min. @ 1200°C to get Li_2ZrO_3 . No mention was made of final product particle size or purity, by the previous authors.

Suiter et al.⁽²⁸⁾ prepared Li_2ZrO_3 from Li_2CO_3 dissolved in an ethylene glycol citric acid mixture and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in H_2O . The solution was evaporated to dryness, and air calcined @ 800°C - 900°C in porcelain crucibles to produce monoclinic Li_2ZrO_3 . Firings @ 700°C or slightly lower were sufficient to remove the organics, but crystalline conversion was incomplete and required higher temperatures. The purity levels were reduced to <500 wppm TMI by the use of high purity (<100 wppm) starting materials. The major problem with the powder was its extreme hygroscopic nature due to high levels of residual chlorine. To remove this obstacle, zirconyl nitrate ($\text{ZrO}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$) was substituted for the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as the Zr source. The powder produced had a particle size variance of 25-5 μm and was reduced to <5 μm by ball milling for 24-48 hours. An Al_2O_3 jar and grinding media were used with only ≈ 100 wppm pick-up of Al_2O_3 by the powder during the milling.

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3.0 CRYSTALLINE PROPERTIES

3.1 INTRODUCTION

A material's phase stability with temperature and/or stoichiometry is an important consideration in the selection of solid breeder compounds. Temperature induced phase changes are of concern if they are accompanied by significant volume changes, which could lead to severe cracking in a sintered body. Due to lithium burn-up, a shift in stoichiometry is expected during the lifetime of the blanket. Any subsequent effect of this deviation would have to be taken into account in the blanket's operating limits or design. One example would be the formation of a liquid phase in the breeder which could lead to enhanced grain growth due to sintering. The increase in grain growth could in turn affect bulk tritium diffusion thus increasing tritium inventories.

3.2 Li-O SYSTEM

Two stable compounds, Li_2O (1) and Li_2O_2 (1), and two metastable compounds LiO_2 (2) and Li_3O_2 (3) have been reported in the Li-O system. LiO_2 was prepared only under controlled conditions and not considered a stable compound at room temperature. Li_3O_2 was the result of the decomposition of anhydrous LiOH under 10^{-5} torr @ 360°C for 48 hours. Stecura (3) was also able to produce the substance at temperatures up to 730°C before Li_2O became the final product. Li_2O_2 was studied extensively by Foppl(4) and Rode et al. (5) who found that Li_2O_2 can exist in two crystalline modifications: (1) $\alpha\text{-Li}_2\text{O}_2$, which is stable up to 225°C , and (2) $\beta\text{-Li}_2\text{O}_2$ which decomposes at $315^\circ\text{-}350^\circ\text{C}$. The remaining compound of this system, Li_2O , possesses a relatively high melting point ($> 1400^\circ\text{C}$) and a high lithium atom density, thus making a most attractive solid breeding oxide material. Although a Li-O phase diagram has not been completed, phase diagrams do exist for Li_2O 's major phase contaminants, Li_2CO_3 and LiOH .

The $\text{Li}_2\text{CO}_3\text{-Li}_2\text{O}$ has been investigated by two investigators (6, 7) with differing results. Papin et al.(6) constructed the phase diagram, Figure 3.2.1,

13-6098

FIGURE 3.2.1 PARTIAL PHASE DIAGRAM OF THE SYSTEM Li_2CO_3 - Li_2O
ACCORDING TO PAPIN et al. (6)

revealing a eutectic @ 87 wt% Li_2O at 428°C . Compositions with less than 20 wt% Li_2O were not examined in this study. Smirnov et.al.⁽⁷⁾ also reported a eutectic but at 705°C for 4 wt% Li_2O in their phase diagram, Figure 3.2.2. In both diagrams, no intermediate compounds in the Li_2CO_3 - Li_2O system are reported but the point of liquid phase formation and its extent remains in some doubt. A projected phase diagram of the system LiOH - Li_2O , Figure 3.2.3, was presented at a Department of Energy sponsored workshop on Solid-Tritium Breeders⁽⁸⁾ by General Atomic. The diagram is an estimation by Dr. J. Norman based on his work with activity coefficients for LiOH in Li_2O . A eutectic appears at 480°C for a composition of 82 wt% LiOH /18 wt% Li_2O , and there are intermediate compounds formed.

Despite problems of reactions between Li_2O and various crucible materials, no phase transitions have been reported from room temperature to its melting point. Powder x-ray diffraction studies performed by Swanson and co-workers⁽⁹⁾ revealed a pattern indexed as face centered cubic (fcc) of the antifluorite

13-6099

FIGURE 3.2.2 PARTIAL PHASE DIAGRAM OF THE SYSTEM Li_2CO_3 - Li_2O
ACCORDING TO SMIRNOV et al. (7)

type. In this arrangement, the O atoms are located at the corners and face centers of the cubic unit cell with the lithium atoms occupying the eight tetrahedral sites. Masaki, et.al.⁽¹⁰⁾ have recently proposed a rhombohedral structure in coexistence with the cubic structure and possessing a slightly different lattice parameter. The most widely recognized lattice parameter for Li_2O is $a=4.6114\text{\AA}$ for the fcc structure, with the rhombohedral structure having an $a=4.610\text{\AA}$ and $\alpha=90.16^\circ$. Some crystalline data for Li_2O has been listed in Figure 3.2.4.

13-6103

FIGURE 3.2.3 PROJECTED PHASE DIAGRAM OF THE SYSTEM LiOH-Li₂O

Figure 3.2.4

Name:	Lithium Oxide		
Formula:	Li ₂ O		
Molecular Weight:	29.88		
Density (g/cm ³ @ 298 K):	2.01		
Lithium Atom Density (g/cm ³):	0.94		
Crystalline Phase(s):	Single phase	(Ref. 11)	
Crystalline Structure(s):	Face-centered cubic	(Ref. 9)	
	Rhombohedral	(Ref. 10)	
Crystalline Parameters (Å):	a = 4.6114	(Ref. 11)	
	a = 4.619	(Ref. 12)	
	a = 4.610	(Ref. 10)	
	α = 90.16°		
Atomic Distance (Å):	Li-O	2.00	(Ref. 13)
	Li-Li	2.32	
	O-O	3.27	
Space Group:	Fm3m	(Ref. 11)	
Atoms per unit cell:	Li	8	
	O	4	
X-Ray Diffraction	Li ₂ O		
JCPDS # 12-254 -(Cubic)	(Ref. 9)		
d _{hkl}	I/I ₀	hkl	
2.664	100	111	
2.306	8	200	
1.6307	40	220	
1.3906	16	311	
1.1531	4	400	
1.058	4	331	
0.9413	8	422	
0.8875	4	511	
0.8151	4	440	
0.7794	6	531	

3.3 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM

Four intermediate compounds have been reported in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ system: Li_5AlO_4 , Li_3AlO_3 , LiAlO_2 and LiAl_5O_8 . Li_3AlO_3 was observed by LaGinesta et.al.⁽¹⁴⁾ to be unstable above 400°C and was not actively pursued. Similarly, LiAl_5O_8 while possessing an attractively high melting point ($>1900^\circ\text{C}$) has such a low lithium atom density (0.09 g/cm^3) that it too will not be considered here, leaving Li_5AlO_4 and LiAlO_2 as viable candidates.

A phase diagram of the $\text{LiAlO}_2-\text{Al}_2\text{O}_3$ system, taken from the work of Lejus and Collonques, is shown in Figure 3.3.1. A complete phase diagram of the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ system has not been accomplished. Although the phase diagram only depicts two phases for LiAlO_2 , three have been reported: α , β , and γ . Chang and Margrave⁽¹⁶⁾ synthesized $\beta\text{-LiAlO}_2$ at 370°C and a pressure 18 kbars, as did Dorhofer⁽¹⁷⁾ in order to reindex the $\beta\text{-LiAlO}_2$ powder diffraction pattern. Although stable at room temperature, subsequent heating to 710°C in air led to an irreversible transformation to $\gamma\text{-LiAlO}_2$. The γ -phase was at first thought to be stable only up to 600°C by Lehmann and Hesselbarth⁽¹⁸⁾ because of their ability to produce $\alpha\text{-LiAlO}_2$ from a solid state reaction of Li_2CO_3 and $\alpha\text{-Al}_2\text{O}_3$ @ 600°C and not above. However, Lejus and Collonques⁽¹⁵⁾ used

13-6102

FIGURE 3.3.1 PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{O} - \text{Al}_2\text{O}_3$

dilatometer measurements to pinpoint the α - γ transition temperature of 900°C , on their phase diagram. In actuality, the α - γ transformation is a sluggish, irreversible structural rearrangement that can occur anywhere between 600° and 900°C , depending upon the rate of heating, time at temperature, and character at the starting powder. As previously stated, the α - γ transition was found to be irreversible, however, Marezio and Remeika⁽¹⁹⁾ subjected a sample of $\gamma\text{-LiAlO}_2$ to a pressure of 35 kbar @ 850°C and then quenched to room temperature and found $\alpha\text{-LiAlO}_2$ had formed. Hummer, et.al.⁽²⁰⁾ reported a rapid reversible inversion for $\gamma\text{-LiAlO}_2$ between 1200° - 1300°C .

Any loss of Li_2O from LiAlO_2 results in a shift in stoichiometry toward the $\text{LiAl}_{5/8}\text{O}_8$ composition. A eutectic is indicated at 1650°C for a composition of 43 mole % Li_2O and 57 mole % Al_2O_3 . At temperatures below $\approx 1650^{\circ}\text{C}$, there exists a solid solution of LiAlO_2 and $\text{LiAl}_{5/8}\text{O}_8$ phases. The compound $\text{LiAl}_{5/8}\text{O}_8$ is a dimorphous spinal-like structure with an ordered and disordered form depending on the temperature. A conversion temperature of 1290°C has been established by Lejus and Collonques⁽¹⁵⁾ for conversion for the low temperature ordered form to the high temperature disordered form. Liquid phases become apparent if the temperature exceeds $\approx 1650^{\circ}\text{C}$ for compositions of $\gamma\text{-LiAlO}_2$ and disordered $\text{LiAl}_{5/8}\text{O}_8$. Relationships for the Li_2O rich side of LiAlO_2 have not been established.

The crystallographic data for LiAlO_2 is presented in Figure 3.3.2. The α -phase possesses a higher density than the γ -phase and, consequently, a higher lithium atom fraction and would be more desirable from a neutron capture standpoint except for the irreversible phase transformation. The crystal structure of $\alpha\text{-LiAlO}_2$ can be described as a distorted super-lattice of an NaCl arrangement where both cations (Li & Al) are in octahedral coordination. In $\gamma\text{-LiAlO}_2$, the cations are in tetrahedral coordination and can be considered an infinite three-dimensional array of distorted tetrahedra, with aluminum and lithium atoms at the center and oxygen atoms at the vertices. Each tetrahedron shares one of its edges with another tetrahedron of a different kind, and each vertex of every tetrahedron is shared with two additional tetrahedron, one of each kind.

Figure 3.3.2

Name:	Lithium Metaaluminate		
Formula:	LiAlO ₂		
Molecular Weight:	65.92		
Density (g/cm ³ @ 298 K)	3.40	α-phase	
	2.68	β-phase	
	2.55	γ-phase	
Lithium Atom Density (g/cm ³):	0.36	0.28	0.27
	α-phase	β-phase	γ-phase
Crystalline Phase(s):	α-phase - only stable to 6000-900°C when irreversible transformation to γ-phase occurs		
	β-phase - high pressure, polymorph - only stable to 710°C when irreversible transformation to γ-phase occurs		
	γ-phase - high temp. phase - stable from room temperature to its melting point		
Crystalline Structure(s):	α-phase - HEXAGONAL		
	β-phase - ORTHORHOMBIC		
	γ-phase - TETRAGONAL		
Lattice Parameters (Å):	α-phase	a = 2.801	(Ref. 19)
		c = 14.216	
	β-phase	a = 5.283	(Ref. 17)
		b = 6.306	
		c = 4.908	
	γ-phase	a = 5.169	(Ref. 21)
Atomic Distance (Å):	Li-O	2.12	2.00
	Al-O	1.90	1.76
		α-phase	β-phase
		(Ref. 19)	(Ref. 21)
Space Group:	R3m	α-phase	(Ref. 19)
		β-phase	
	P422	γ-phase	(Ref. 21)
Atoms per Unit Cell:	Li	3	4
	Al	3	4
	O	6	8
		α-phase	β-phase

Figure 3.3.2 (Continued)

X-Ray Diffraction:

α -LiAlO ₂		
JCPDS Card #19-713 - (HEXAGONAL)	(Ref. 19)	
d_A^o	I/I _o	hkl
4.72	70	003
2.386	40	101
2.000	100	104
1.844	5	015
1.556	40	107
1.432	60	018
1.399	60	110
1.342	40	113
1.226	5	1010
1.208	10	021
1.184	40	0012
1.148	60	024

β -LiAlO ₂		
(ORTHORHOMBIC)	(Ref. 17)	
d_A^o	I/I _o	hkl
4.05	100	110
3.87	100	010
3.12	30	111
2.706	100	120
2.639	60	200
2.452	100	022
2.368	30	121
2.178	10	211
2.096	20	112
1.818	30	122
1.798	20	202
1.604	20	311
1.576	30	040
1.539	60	320
1.402	30	123
1.391	20	203
1.303	30	322

Figure 3.3.2 (Continued)

γ -LiAlO ₂		
JCPDS Card #18-714-(TETRAGONAL)	(Ref. 21)	
d_{hkl}^0	I/I ₀	hkl
3.98	100	101
3.65	40	110
3.15	50	111
2.677	90	102
2.584	90	200
2.388	5	201
2.168	30	211
1.937	5	103
1.860	50	212
1.827	30	220
1.814	30	113
1.658	5	301
1.633	30	310
1.624	5	203
1.580	30	311
1.565	40	004
1.508	80	302
1.440	5	114
1.396	10	321
1.376	5	223
1.339	50	204
1.303	70	322
1.297	5	214
1.286	50	313
1.265	5	401
1.253	5	410
1.229	30	411
1.218	70	330, 105
1.195	5	331, 402
1.189	30	224
1.182	10	323
1.156	10	420

Although γ -LiAlO₂ is a less dense phase and thus has a lower lithium atom density, it is normally considered a more practical solid breeding material because of its phase stability and ease of manufacture and fabricability.

The compound, Li₅AlO₄, while not depicted in Figure 3.3.1, has been studied by Guggi et al. (22) as a solid breeder candidate. The major attractive feature is its lithium atom density of $\approx 0.62 \text{ g/cm}^3$, which is higher than that of most

solid breeders except for Li_2O and Li_8ZrO_6 . On the other hand, its major drawbacks are the low melting point (1047°C) which reduces the possible operating limits and a phase transformation near 800°C . $\alpha\text{-Li}_5\text{AlO}_4$ is the low temperature phase and is stable to $\approx 800^\circ$ where it undergoes an irreversible phase transformation to $\beta\text{-Li}_5\text{AlO}_4$. The β -phase was found to be stable from room temperature to its decomposition triple point of 1047°C .

The crystallographic data for both α - and $\beta\text{-Li}_5\text{AlO}_4$ is contained in Figure 3.3.3. $\alpha\text{-Li}_5\text{AlO}_4$ is isostructural with $\alpha\text{-Li}_5\text{GaO}_4$ and is a superstructure of Li_2O with scattered AlO_4 groups and vacancies in the cation lattice. The Al^{3+} cations are octahedral coordination while the Li^+ cations reside in tetrahedral coordination. The $\beta\text{-Li}_5\text{AlO}_4$ crystal structure is somewhat different in that both cations are in tetrahedral coordination with each tetrahedral being shared at two corners with another tetrahedra containing an opposite cation.

Figure 3.3.3

Name:	Tetraoxo-Lithium-Aluminate		
Formula:	Li ₅ AlO ₄		
Molecular Weight:	125.67		
Density (g/cm ³ @ 298 K):	2.25	α-phase	
	2.22	β-phase	
Lithium Atom Density (g/cm ³):	0.62	0.61	
	α-phase	β-phase	
Crystalline Phase(s):	α-phase:	low temp-phase - stable up to 750°-800°C	
	β-phase:	high temp-phase - stable from room temp. to decomposition point	
Crystalline Structure(s):	α-phase - ORTHORHOMBIC		
	β-phase - ORTHORHOMBIC		
Crystalline Parameters (Å):	α-phase	a = 9.087	(Ref. 23)
		b = 8.947	
		c = 9.120	
	β-phase	a = 6.42	(Ref. 24)
		b = 6.30	
		c = 4.62	
Atomic Distance (Å):	Li-O	unreported	3.34
	Al-O	"	3.36
		α-phase	β-phase
Space Group:	Pbca	α-phase	(Ref. 23)
	Pmmn	β-phase	(Ref. 24)
Atoms per Unit Cell:	Li	40	10
	Al	8	2
	O	32	8
		α-phase	β-phase

Figure 3.3.3 (Continued)

X-Ray Diffraction:

α -Li ₅ AlO ₄		
JCPDS Card #24-596-(ORTHORHOMBIC)		(Ref.23)
⁰ dÅ	I/I ₀	hkl
5.23	18	111
4.56	2	200
4.08	35	102
4.06	7	210
4.02	30	021
3.71	50	112, 211
3.01	3	221
2.748	6	113
2.707	2	131
2.612	100	222
2.515	5	023
2.493	3	230
2.431	13	213, 312
2.407	5	132, 231
1.961	3	142
1.926	12	332
1.784	4	314, 413
1.774	4	134, 431
1.742	4	333
1.684	6	423, 234
1.609	20	404
1.596	16	044
1.594	20	440

β -Li ₅ AlO ₄		
JCPDS Card #31-703-(ORTHORHOMBIC)		(Ref. 24)
⁰ dÅ	I/I ₀	hkl
4.51	60	110
3.760	70	101
3.731	40	011
2.639	80	201
2.605	100	021
2.433	30	211
2.415	40	121
2.056	10	112
1.944	50	301
1.914	10	031
1.791	30	122
1.612	90	222
1.606	10	400
1.577	30	040
1.524	10	312
1.454	20	141
1.390	10	203
1.368	20	421

3.4 $\text{Li}_2\text{O}-\text{SiO}_2$ SYSTEM

There have been five reported compounds in the $\text{Li}_2\text{O}-\text{SiO}_2$ system: $\text{Li}_6\text{Si}_2\text{O}_7$, Li_4SiO_4 , Li_2SiO_3 , $\text{Li}_2\text{Si}_2\text{O}_5$ and $\text{Li}_2\text{Si}_3\text{O}_7$. Of these, $\text{Li}_6\text{Si}_2\text{O}_7$ and $\text{Li}_2\text{Si}_3\text{O}_7$ have been found to be metastable and will not be extensively discussed here.

Völlenkle et al.⁽²⁵⁾ reported the formation of $\text{Li}_6\text{Si}_2\text{O}_7$ by rapidly quenching to room temperature a 3 Li_2O : 2 SiO_2 melt @ 1300°C in air. They found that by cooling slowly from 1300°C, no $\text{Li}_6\text{Si}_2\text{O}_7$ formed but rather Li_4SiO_4 and Li_2SiO_3 . In addition, if the quenched $\text{Li}_6\text{Si}_2\text{O}_7$ material was reheated to 900°C for several hours, it would again form Li_4SiO_4 and Li_2SiO_3 phases with no trace of the original $\text{Li}_6\text{Si}_2\text{O}_7$.

West and Glasser⁽²⁶⁾ produced $\text{Li}_2\text{Si}_3\text{O}_7$ from 1 Li_2O : 3 SiO_2 melt by cooling from 1400°C to 890°C and then to room temperature. If cooled directly from 1400°C to room temperature only $\text{Li}_2\text{Si}_2\text{O}_5$, SiO_2 and glass were seen. Although stable at ambient temperatures, $\text{Li}_2\text{Si}_3\text{O}_7$ was destroyed by prolonged heating (12-24 hours) above 650°C. The decomposition products were SiO_2 and $\text{Li}_2\text{Si}_2\text{O}_5$.

Kracek⁽²⁷⁾ developed a partial phase diagram (Figure 3.4.1) concerning the three stable phases: Li_4SiO_4 , Li_2SiO_3 and $\text{Li}_2\text{Si}_2\text{O}_5$. Of these, lithium disilicate, $\text{Li}_2\text{Si}_2\text{O}_5$, has been the most extensively studied since it is widely used in glass-ceramic applications.⁽²⁸⁻³⁰⁾ Unfortunately, it possesses both a low melting point (1033°C) and lithium atom density (0.22 g/cm³) and has not been actively considered as a solid breeder. The remaining two materials, lithium orthosilicate (Li_4SiO_4) and lithium metasilicate (Li_2SiO_3), have received consideration.

Figure 3.4.1 reveals that Li_4SiO_4 decomposes at 1255°C rather than merely melting and that a loss of Li_2O from Li_4SiO_4 allows liquid phase formation at 1024°C. Li_2SiO_3 melts at 1201°C and any loss or gain of Li_2O will result in some liquid phase formation at 1033°C and 1024°C respectively.

This diagram does not show any phase transitions for either Li_4SiO_4 or Li_2SiO_3 but West and Glasser^(31,32) reported a crystallographic transformation for

13-6104

FIGURE 3.4.1 PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{O} - \text{SiO}_2$

Li_4SiO_4 @ 666°C . Although studying the $\text{Li}_4\text{SiO}_4 - \text{Zn}_2\text{SiO}_4$ system, they used DTA and high temperature x-ray diffraction to identify a transformation in "pure" Li_4SiO_4 . Their results indicate a reversible transformation accompanied by a crystal change which usually is a severe volume change for the material. This transformation process would severely limit the usefulness of a sintered, Li_4SiO_4 body without crack initiation. Their paper did not mention the chemical or phase purity of the Li_4SiO_4 used in their study, which could have affected their results. The work presented by Hollenberg⁽³³⁾ on a Li_4SiO_4 sample slightly contaminated with Li_2SiO_3 indicated a reversible transformation @ 665°C but one that was displacive instead of crystallographic. Displacive transformations require some movement or rotation of atoms within the structure but don't result in a large volume change that occurs during crystallographic transformations. This finding allayed fears of a phase change which

would crack a sintered, Li_4SiO_4 body when heated beyond the transformation temperature.

Crystallographic information concerning Li_4SiO_4 is listed in Figure 3.4.2. The lattice parameters of monoclinic Li_4SiO_4 have been determined by numerous investigators.⁽³⁵⁻³⁷⁾ Most are fairly close except for Tranqui et al.⁽³⁴⁾ who used a super lattice to explain some of the slight irregularities seen by earlier investigators. The Li_4SiO_4 crystal structure contains isolated $[\text{SiO}_4]$ tetrahedra being connected by edge and corner sharing with $[\text{LiO}_4]$, $[\text{LiO}_5]$, and $[\text{LiO}_6]$ polyhedra. The positions of the lithium atoms are only partially occupied. Tranqui et al.⁽³⁴⁾ expanded the unit cell to include 14 Li_4SiO_4 formula units instead of the previously described 2 Li_4SiO_4 formula units to eliminate differences between earlier investigators. The higher temperature form of Li_4SiO_4 proposed by West and Glasser⁽³²⁾ has been classified as pseudo-orthorhombic but is fairly close to being tetragonal. Hollenberg's⁽³³⁾ high temperature x-ray diffraction patterns revealed that the transformation on the Li_4SiO_4 crystal structure involved a slight distortion of atoms in the lattices without breaking any bonds. Above the transformation temperature, he found that the c parameter decreased while the a and b lattice parameters increased, thus allowing the high temperature phase to be merely a derivative of the starting material with only a small volume change.

Lithium metasilicate, Li_2SiO_3 , has a slightly lower melting point (1201°C) than that of Li_4SiO_4 and a lower lithium atom density (0.39 g/cm^3) but undergoes no phase transitions during the path to its melting point. Figure 3.4.3 contains its available crystallographic data. The crystal structure for Li_2SiO_3 can be described as $[\text{SiO}_4]$ tetrahedra forming chains parallel to the c-axis with two tetrahedra in the unit cell. The tetrahedra are joined at the corners with the lithium atoms linking the chains together in the a and b directions. This positioning results in the lithium atoms being in tetrahedral coordination.

Figure 3.4.2

Name:	Lithium Orthosilicate				
Formula:	Li_4SiO_4				
Molecular Weight:	119.84				
Density (g/cm^3 @ 298 K):	2.39	α -phase			
	2.21	γ -phase			
Lithium Atom Density (g/cm^3):	0.55	0.51			
	α -phase	γ -phase			
Crystalline Phase(s):	α -phase - low temp. phase - stable until reversible displacive transformation @ 665°C (Ref. 33)				
	γ -phase high temp. phase - stable only above 665°C				
Crystalline Phase(s):	α -phase; MONOCLINIC				
	γ -phase; PSEUDO-ORTHORHOMBIC				
Crystalline Structure(s):	α -phase; MONOCLINIC				
	γ -phase; PSEUDO-ORTHORHOMBIC				
Crystalline Parameters ($\text{\AA}$):	α -phase				
a	11.546	5.14	5.296	5.25	5.16
b	6.090	6.10	6.099	6.15	6.12
c	16.645	5.30	5.148	5.33	5.30
β	99.5	90.5	90.31	91.0	90.1
	(Ref.34)	(Ref.35)	(Ref.34)	(Ref.36)	(Ref.37)
	γ -phase				
a	5.30	5.23	5.24		
b	6.32	6.32	6.14		
c	5.45	5.45	5.52		
β	90.8	90.35			
	(Ref.32)	(Ref.38)	(Ref.38)		
Atomic Distance ($\text{\AA}$):	Si-O	1.632			
	Li-O	1.975	Li coord. #4		
		2.099	5		
		2.247	6		
		α -phase			
		(Ref. 35)			
Space Group:	$P2_1/m$	α -phase	(Ref. 35)		
		γ -phase			
Atoms per Unit Cell:	Li	8	56	8	
	Si	2	14	2	
	O	8	56	8	
		α -phase	α -phase	γ -phase	
		(Ref.35)	(Ref.34)		

Figure 3.4.2 (Continued)

X-Ray Diffraction:

$\alpha\text{-Li}_4\text{SiO}_4$

JCPDS Card #20-637 - (MONOCLINIC) (Ref.39)

dÅ	I/I _o	hkl
5.29	30	100
5.15	20	001
4.00	100	110
3.93	80	011
3.70	10	101
3.68	45	101
3.16	55	111
3.05	16	020
2.645	100	200, 120
2.623	25	021
2.574	55	022
2.431	4	210
2.352	30	121, 201
2.321	<2	102
2.193	10	211
2.161	2	112
2.033	2	030
2.001	2	220
1.967	2	022
1.898	2	130
1.866	8	221
1.846	18	122
1.841	10	122, 202
1.782	16	131, 131
1.765	2	300
1.762	2	212
1.716	2	003
1.695	2	310
1.667	4	301
1.652	2	013
1.630	4	103
1.613	4	311, 230
1.580	6	113
1.575	4	113, 222
1.540	2	231
1.526	30	132, 320
1.496	8	023
1.465	4	140, 321
1.441	4	123

There were 11 more d-spacings with relative intensities (I/I_o) <10.

Figure 3.4.3

Name:	Lithium Metasilicate		
Formula:	Li_2SiO_3		
Molecular Weight:	89.96		
Density (g/cm^3 @ 298 K):	2.53		
Lithium Atom Density (g/cm^3):	0.39		
Crystalline Phase(s):	Single phase		
Crystalline Structure(s):	ORTHORHOMBIC		
Crystalline Parameters ($\text{\AA}$):			
	a	5.3975	9.392 5.43
	b	9.3974	5.397 9.41
	c	4.6615	4.660 4.66
		(Ref. 40)	(Ref. 41) (Ref. 42)
Atomic Distance ($\text{\AA}$):			
	Li-O	2.00	
	Si-O	1.636	
		(Ref. 41)	
Space Group:	Cmc2 ₁		(Ref. 41)
Atoms per Unit Cell:	Li	8	(Ref. 42)
	Si	4	
	O	12	

Figure 3.4.3 (Continued)

X-Ray Diffraction:

Li_2SiO_3		
JCPDS Card #29-828- (ORTHORHOMBIC) (Ref.40)		
dÅ	I/I _o	hkl
4.69	100	020, 110
3.301	65	111
2.708	65	130
2.700	45	200
2.342	19	131, 220
2.331	20	002
2.091	7	221
2.085	5	022, 112
1.7747	4	150
1.7667	9	310, 132
1.7638	8	202
1.6563	7	241
1.6522	7	311, 222
1.5665	12	060
1.5605	15	330
1.4747	3	113
1.4105	1	242
1.4079	1	312
1.3547	3	260
1.3475	5	133
1.3001	5	062, 350
1.2965	8	332, 401
1.2544	8	171

19 more reflections to $= 0.9337$ dÅ with
none having $I/I_o > 3$

3.5 Li₂O-TiO₂ SYSTEM

A partial phase diagram of the system Li₂O-TiO₂, shown in Figure 3.5.1, has been constructed from the work of Gicquel et al.,⁽⁴³⁾ Hummel and Tien,⁽⁴⁴⁾ and Mikkelsen, Jr.⁽⁴⁵⁾ Although not all indicated on the diagram, numerous Li₂O-TiO₂ compounds have been reported: Li₄TiO₄, Li₂TiO₃, LiTiO₂, LiTi₂O₄, Li₂Ti₃O₇, Li₄Ti₅O₁₂ and Li₂Ti₂O₅ to name a few. Li₂Ti₃O₇ has been studied by Mikkelsen⁽⁴⁵⁾ who found that it melts @ 1300°C but decomposes eutectoidally @ 940°C. In addition Li₄Ti₅O₁₂ was shown to decompose @ 1000°C. The other materials, LiTiO₂, LiTi₂O₄ and Li₂Ti₂O₅ possess both low melting points and lithium atom densities and will not be considered further.

According to Figure 3.5.1, Li₄TiO₄ decomposes @ 1200°C to Li₂TiO₃ and a liquid, while any additions of Li₂O to Li₄TiO₄ lower the temperature of initial liquid phase formation to 1030°C. A eutectic exists at ~1030°C for a composition of 56 wt % Li₂O and 44 wt % TiO₂. Also indicated by the phase diagram is the α to β phase transformation for Li₄TiO₄ @ 670°C. Dubey and West⁽⁴⁶⁾ found the α to β transformation to be reversible according to DTA results and with little volume change. The crystallographic data for Li₄TiO₄ is contained in Figure 3.5.2. The structure is built up by [TiO₄] tetrahedra being linked together by [LiO₄] tetrahedra, so both Li and Ti atoms are tetrahedrally coordinated by oxygen and all sites are fully occupied.

Although not extensively studied, Dubey and West⁽⁴⁶⁾ believed that β-Li₄TiO₄ possessed a structure similar to the low temperature form of Li₄SiO₄ where the degree of occupancy by Li atoms has changed as well as their coordinating numbers with [LiO₄], [LiO₅] and [LiO₆] existing.

While Li₂TiO₃ has been found to melt @ 1535°C, any shift in stoichiometry results in a liquid phase formation at lower temperatures. Increasing the Li₂O concentration of Li₂TiO₃ will result in some liquid being formed at 1200°C while a Li₂O loss produces a liquid phase @ 1300°C. A reversible β to γ phase transformation occurs at 1150°C although, in reality, Li₂TiO₃ has been found to have three allotropes: α, β, and γ. The α-phase was studied by Gicquel et al.,⁽⁴³⁾ who found it to be only a metastable version which transforms to β-Li₂TiO₃ upon heating above 300°C. The β-phase was found to be stable

13-6106

FIGURE 3.5.1 PARTIAL PHASE DIAGRAM OF THE SYSTEM $\text{Li}_2\text{O} - \text{TiO}_2$

Figure 3.5.2

Name:	Lithium Orthotitanate		
Formula:	Li_4TiO_4		
Molecular Weight:	139.65		
Density (g/cm^3 @ 298K);	2.57	α -phase	β -phase
Lithium Atom Density (g/cm^3):	0.51	α - phase	β -phase
Crystalline Phase(s):	α -phase; stable until reversible transformation @ 670 (Ref. 47) β -phase; only stable above 670°C		
Crystalline Structure(s):	α -phase; ORTHORHOMBIC β -phase		
Crystalline Parameters ($\text{\AA}$):	α -phase	a = 7.91 (Ref. 47) b = 6.15 c = 7.41	
	β -phase	Not reported	
Atomic Distance ($\text{\AA}$):	Ti-O	1.77	
	Li-O	1.98	
		α -phase	β -phase
		(Ref. 48)	
Space Group:	Bmmb	α -phase	(Ref. 47)
		β -phase	
Atoms per Unit Cell:	Li	16	
	Ti	4	
	O	16	
		γ -phase	β -phase
		(Ref. 48)	

Figure 3.5.2 (Continued)

X-Ray Diffraction Data:

α -Li₄TiO₄
JCPDS Card #26-1197-(ORTHORHOMBIC) (Ref. 47)

dÅ	I/I ₀	hkl
5.41	50	101
4.07	50	111
3.95	30	200
3.71	10	002
3.18	40	012
3.07	20	020
2.71	100	202
2.67	50	121
2.47	20	212
2.42	10	220
2.36	10	103
2.31	30	311
2.21	10	113
1.976	20	400
1.914	20	131
1.873	30	123
1.805	20	303
1.750	10	402

to 1150°C where the reversible γ -transformation occurs. Detailed high temperature work has not been done on the γ -phase so an x-ray pattern is not known. The β -phase of Li₂TiO₃ is considered to be a derivative of the NaCl structure, with the oxygen atoms occupying the Cl ions sites and the lithium and titanium atoms occupying the Na sites in octahedral coordination. Further crystallographic data are listed in Figure 3.5.3. A disagreement exists over the correct x-ray diffraction pattern for β -Li₂TiO₃ between the JCPDS version given by Lang⁽⁵⁰⁾ and Dorrian.⁽⁴⁹⁾ Liebert⁽⁵¹⁾ further refined his measurements and showed that Dorrian's work was the more acceptable. Both Lang's⁽⁵⁰⁾ and Liebert's⁽⁵¹⁾ patterns have been listed for comparison purposes.

Figure 3.5.3

Name:	Lithium Metatitanate				
Formula:	Li ₂ TiO ₃				
Molecular Weight:	109.78				
Density (g/cm ³ @ 298K):	2.00	α-phase			
	3.43	β-phase			
	2.57	γ-phase			
Lithium Atom Density (g/cm ³):	0.25	0.43	0.32		
	α-phase	β-phase	γ-phase		
Crystalline Phase(s):	α-phase - metastable, converts irreversibly to β @ 300°C				
	β-phase - stable from R.T. to 1150°C where a reversible transformation to γ occurs				
	γ-phase - stable above 1150°C				
Crystalline Structure(s):	α-phase - CUBIC				
	β-phase - MONOCLINIC				
	γ-phase - CUBIC				
Crystalline Parameters (Å):	α-phase	a = 4.50	(Ref. 43)		
	β-phase	a = 5.041	5.05		
		b = 8.806	8.76		
		c = 9.726	28.60		
		β = 100°01'	100.0		
		(Ref. 49)	(Ref. 50)		
	γ-phase	a = 4.1355	(Ref. 45)		
Atomic Distance (Å):	Li-O	2.14			
	Ti-O	1.95			
		α-phase	β-phase	γ-phase	
Space Group:	Not reported	α-phase			
	C2/c	β-phase			
	Not reported	γ-phase			
Atoms per Unit Cell:	Li	2	16	40	2
	Ti	1	8 or	27	1
	O	3	24	72	3
		α-phase	β-phase	γ-phase	
		(Ref. 43)	(Ref. 49)	(Ref. 50)	(Ref. 45)

Figure 3.5.3 (Continued)

X-Ray Diffraction:

JCPDS Card #8-249-(MONOCLINIC) (Ref.50)			(MONOCLINIC) (Ref. 51)		
dÅ	I/I ₀	hkl	dÅ	I/I ₀	hkl
4.76	50	006	4.784	71	002
			4.343	28	110
			4.211	11	012
			4.005	16	021
			3.739	6	112
			2.994	6	112
2.481	30	202	2.498	52	200
			2.390	3	004
			2.300	5	201
2.070	100	208	2.072	100	202
1.896	5	20 $\overline{10}$	1.909	15	230
			1.811	4	142
			1.598	29	006
1.592	30	2014, 0018	1.593	29	241
1.463	100	2016, 060	1.465	83	312
1.396	30	066	1.399	17	243
1.257	5	402	1.263	4	304
1.242	5	2020, 0612	1.201	14	226
1.193	75	0024, 408	1.195	19	420
1.157	50	2022, 4010	1.163	11	047

3.6 Li₂O-ZrO₂ SYSTEM

Although no binary phase diagram exists for this system, several compounds have been reported: Li₈ZrO₆, Li₄ZrO₄, Li₂ZrO₃ and Li₂Zr₂O₅. Work performed by Plyushchev and Grizik⁽⁶¹⁾ revealed that Li₂Zr₂O₅ was a metastable product and did not exist under normal conditions. Of the remaining three, only Li₂ZrO₃ has received much interest as a solid breeder.

The crystalline properties of Li₈ZrO₆ have been tabulated in Figure 3.6.1 but the work to date has been fairly limited. Li₈ZrO₆ has been reported by several investigators⁽⁵²⁻⁵⁵⁾ but most have restricted themselves to the study of formation conditions and enthalpies. Larsen⁽⁵⁶⁾ has examined several fused Li₈ZrO₆ samples and concluded that there are no phase transitions from room temperature to its melting point. Obviously since no phase diagram exists, the effect of departures from stoichiometry cannot be described. Of major
(62)

Figure 3.6.1

Name:	Octalithium Zirconate		
Formula:	Li_8ZrO_6		
Molecular Weight:	242.73		
Density (g/cm^3 @ 298 K):	3.01		
Lithium Atom Density (g/cm^3):	0.69		
Crystalline Phase(s):	Single phase		
Crystalline Structure(s):	HEXAGONAL (Ref. 54)		
Crystalline Parameters ($\text{\AA}$):	a = 5.483 (Ref. 54) c = 15.45		
Atomic Distance ($\text{\AA}$):	LiO	2.14	(Ref. 54)
	Zr-O		
Space Group:	$R\bar{3}$		
Atoms per Unit Cell:	Li	24	
	Zr	3	
	O	18	(Ref. 54)

Figure 3.6.1 (Continued)

X-Ray Diffraction:

JCPDS Card #26-867-(HEXAGONAL) (Ref. 57)

5.15	40	003
4.52	100	101
4.04	50	012
2.996	20	104
2.744	3	110
2.583	20	015, 006
2.419	80	113
2.351	13	021
2.268	12	202
2.021	10	024
2.003	10	107
1.875	75	205, 116
1.785	25	018, 211
1.748	18	122
1.716	4	009
1.627	18	214
1.617	9	027
1.583	30	300
1.552	15	125
1.513	11	303
1.498	7	208
1.470	5	1010
1.456	18	119
1.393	11	217
1.371	2	220
1.348	7	306, 0111
1.325	10	223
1.314	16	128, 131
1.300	10	312, 0210
1.287	4	0012
1.248	5	134
1.210	18	315, 226+
1.185	4	401

importance would be the formation of a liquid phase. Troemel and Hauch studied the crystal structure of Li_8ZrO_6 and found it to be isostructural with Li_8SnO_6 . The Zr^{4+} and $1/3$ of Li^+ atoms are octahedral coordinated by O atoms and these layers are separated in the c-direction by the remaining $2/3$ of the Li^+ atoms tetrahedrally coordinated. Delmar, et.al.⁽⁶³⁾ verified this structure during ionic conductivity experiments on Li_8MO_6 ($M = \text{Zr, Sn}$), Li_7LO_6 ($L = \text{Nb, Ta}$) and $\text{Li}_6\text{In}_2\text{O}_6$.

The Li_4ZrO_4 composition has received even less interest than Li_8ZrO_6 . Very little information exists on this material as even its melting point has not been published. The available crystallographic data are listed in Figure 3.6.2.

Li_2ZrO_3 possesses a high melting point (1500°C) with a reversible monoclinic to tetragonal phase transition occurring 1100°C . Since this is above the normal operating temperature limits of the breeding blanket, only the monoclinic form has received any interest. Its crystalline data are contained in Figure 3.6.3. Since there is no phase diagram, the effect of any deviations from stoichiometry of the Li_2ZrO_3 is unclear. The structural arrangement of Li_2ZrO_3 is NaCl-like, with the oxygen atoms form a distorted cubic close-packed network and the cations occupying all octahedral sites present in this network. The cations (Li^+ and Zr^{4+}) are in the ratio 2:1 and are distributed such that any layer perpendicular to the c-axis is the same.

Figure 3.6.2

Name:	Lithium Orthozirconate	
Formula:	Li_4ZrO_4	
Molecular Weight:	182.97	
Density (g/cm^3 @ 298 K):	3.87	
Lithium Atom Density (g/cm^3):	0.59	
Crystalline Phase(s):	Only one reported	
Crystalline Structure(s):	MONOCLINIC	(Ref. 58)
Crystalline Parameters ($\text{\AA}$):	a = 10.446	(Ref. 58)
	b = 5.991	
	c = 10.205	
	$\beta = 100.25^\circ$	
Atomic Distance ($\text{\AA}$):	Not reported	
Space Group:	Cc	
Atoms per Unit Cell:	Li	32
	Zr	8
	O	32
	(Ref. 58)	

Figure 3.6.2 (Continued)

X-Ray Diffraction:

JCPDS Card #20-645-(MONOCLINIC) (Ref. 58)

dÅ	I/I _o	hkl
5.18	30	110
5.14	85	200
4.78	100	111
4.44	2	111
3.96	18	202
3.78	50	112
3.45	20	112
3.31	30	202
2.977	25	310
2.933	12	113
2.870	20	021
2.753	2	312
2.739	2	311
2.702	12	113
2.587	<2	220
2.570	<2	400, 022
2.511	4	004
2.473	6	402
2.454	10	221
2.432	8	204
2.416	2	313
2.401	<2	312
2.343	<2	114
2.232	8	023
2.183	4	114
2.143	90	223
2.138	25	402
2.112	2	204
2.083	6	314
2.070	6	313
1.981	<2	404
1.973	<2	511
1.965	10	421, 223
1.960	2	130
1.945	6	510
1.936	8	131
1.932	2	115
1.926	2	512, 024
1.911	2	131
1.868	4	421

47 additional peaks but only one @ 1.505 has
a relative intensity >20

Figure 3.6.3

Name:	Lithium Metazirconate		
Formula:	Li_2ZrO_3		
Molecular Weight:	153.10		
Density (g/cm^3 @ 298 K):	(monoclinic) 4.15 (tetragonal) 3.67		
Lithium Atom Density (g/cm^3):	(monoclinic) 0.38 (tetragonal) 0.33		
Crystalline Phase(s):	Monoclinic; only stable until 1100°C Tetragonal; only stable above 1100°C		
Crystalline Structure(s):	MONOCLINIC TETRAGONAL		
Crystalline Parameters ($\text{\AA}$):	MONOCLINIC	a = 5.427 b = 9.025 c = 5.427 $\beta = 112.75^\circ$ (Ref. 59)	5.422 9.022 5.419 112.709 (Ref. 64)
	TETRAGONAL	a = 8.98 c = 3.42	(Ref. 60)
Atomic Distance ($\text{\AA}$):		Avg.	
	Li-Zr	3.06	
	Li-O	2.22	
	Zr-O	2.10	
		MONO. (Ref. 59)	
Space Group:	C2/C	MONOCLINIC TETRAGONAL	(Ref. 64)
Atoms per Unit Cell:	Li	8	8
	Zr	4	4
	O	12	12
		Monoclinic	Tetragonal

Figure 3.6.3 (Continued)

X-Ray Diffraction:

JCPDS Card #23-372-(MONOCLINIC) (Ref. 59)

dÅ	I/I _o	hkl
4.52	60	020
4.38	100	110
4.04	80	111
3.34	80	021
2.853	60	111
2.58	70	112, 130
2.505	70	131, 200
2.314	60	221
2.259	80	040, 202
2.189	40	220, 022
2.127	80	131
2.058	60	041
2.020	40	222
1.911	60	112
1.794	60	221
1.770	40	311
1.729	40	241
1.698	80	312, 150
1.675	60	151, 240
1.641	40	310, 132
1.616	60	223
1.596	40	242
1.563	60	023
1.548	80	133, 331

Figure 3.6.3 (Continued)

Li_2ZrO_3
(TETRAGONAL) (Ref. 60)

$d\text{\AA}$	I/I ₀	hkl
4.48	10	200
3.98	40	210
3.42	10	001
2.832	30	310
2.491	60	320
2.249	50	400, 301
2.114	100	330
1.674	20	102
1.597	10	202
1.542	90	530
1.503	70	222
1.477	10	610
1.405	10	531
1.249	80	631
1.126	10	602
1.002	30	722

NOTE: Only slight differences in the $d\text{\AA}$ spacings exist between the above data and those reported on JCPDS #20-647 although both come from the same reference.

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4.0 THERMAL PROPERTIES

4.1 INTRODUCTION

The candidate breeders' response to temperature are important to the viability of proposed blanket designs. Critical properties include melting points, vaporization rates, thermal conductivity, specific heat and thermal expansion.

The solid breeder's melting point has influenced the upper-most operating limit in blanket designs. In general, $\approx .6 T_{m.p.}$ has been suggested as an upper bound due to sintering and grain growth at temperatures above this. The main concerns have involved the lengthening of the path for tritium bulk diffusion by grain growth and pore closure. This concern, however, has never been fully justified and while grain growth may occur at the higher temperatures, the increase in tritium diffusion kinetics may offset the longer path length and pore closure.

Vaporization rates become important as higher temperatures are reached or if the solid breeder is in contact with metal. Although most of the data has been generated using Pt knudsen cells, trends are still apparent. In actual blanket operation, Li transport, in some form, is more likely to occur from the "hotter" areas to "cooler" ones but still stay within the pellet or body itself rather than being deposited on metal surfaces or leaving in a purge gas stream.

Thermal conductivity values are needed to predict the coolant flows necessary to keep the solid breeder's temperature within the desired limits. The effect of irradiation (i.e. swelling, microcrack, etc.) may alter this property and will have to be taken into account. Presently, no post irradiation thermal conductivity measurements have been made on solid tritium materials although some have been planned.

Specific heat data are required to convert thermal diffusivity into more usable thermal conductivity values. In general, specific heats for ceramic systems increase from a low value at low temperatures to a value near 5.96 cal/g-atom $^{\circ}\text{C}$ at temperatures in the neighborhood of 1000 $^{\circ}\text{C}$. Further increases in

temperature do not strongly affect this value unless there are phase transitions, which result in abrupt changes in the specific heat curve.

Thermal expansion data are used in coolant calculations whereby the solid breeder is cooled to maintain desired, predictable, operating temperatures. If the solid breeder is encapsulated and cooled by being in contact with "cooled" metal, then it becomes important to know if the ceramic will "pull away" from the metal as both expand and lose cooling efficiency. If gap cooling is employed, the thermal expansions of both metal and ceramic are examined to insure there is a sufficient distance between solid breeder and metal to allow the coolant gas to be effective.

4.2 MELTING POINT

A major disagreement over the exact melting point of a solid breeder candidate, Li_2O , has existed for many years. The reporting of values from 1427°C to 1732°C ⁽¹⁻⁷⁾ resulted in considerable uncertainty as to its exact melting point. The wide variance has probably been the result of the extremely reactive nature of Li_2O at high temperatures with crucible materials, introduction of impurities (metallic or LiOH) or just estimations on the part of the authors. Recently, several investigators⁽⁴⁻⁶⁾ have proposed melting points for Li_2O ranging from 1430° to 1438°C , which are close to the 1427°C proposed by Brewer and Margrave⁽³⁾. For this study, the figure $1432 \pm 6^\circ\text{C}$ has been adopted as an average value derived from the latest investigators. The melting points for some of the solid breeder materials have been listed in Figure 4.2.1.

4.3 VAPORIZATION

4.3.1 Li_2O

Ikeda et al.⁽⁸⁾ has obtained the vapor pressure of Li_2O by high temperature mass spectrometry using a Pt Knudsen cell. The Li partial pressure, illustrated in Figure 4.3.1.1, was in fairly good agreement with the findings of Kudo et al.⁽⁹⁾ over the same temperature regime. Their results have been

Figure 4.2.1 Melting Points of Solid Breeder Candidates

<u>MATERIAL</u>	<u>M.P. (°C)</u>	<u>COMMENTS</u>
Li ₂ O	1432±6	Avg. of values reported (1427, 1430, 1432, 1438)
β-Li ₅ AlO ₄	1047	Decomposes/Triple Point
γ-LiAlO ₂	1610	
LiAl ₅ O ₈	1950	
Li ₄ SiO ₄	1255	Decomposes
Li ₂ SiO ₃	1201	
Li ₂ Si ₂ O ₅	1033	
Li ₄ TiO ₄	1200	Decomposes
Li ₂ TiO ₃	1535	
Li ₈ ZrO ₆	1295	
Li ₄ ZrO ₄	Unknown	
Li ₂ ZrO ₃	1600	

listed below with P_{Li} being given in Pascals:

Ikeda et al.⁽⁸⁾ $T = 1316$ to 1603 K

$$\log P_{Li} = -(19.02 \times 10^3/T) + 12.22 \quad (15)$$

Kudo et al.⁽⁹⁾ $T = 1352$ to 1663 K

$$\log P_{Li} = -(18.19 \times 10^3/T) + 12.09 \quad (16)$$

In addition, Ikeda et al.⁽⁸⁾ reported partial pressures for O₂ and Li₂O while Kudo et al.⁽⁹⁾ detected pressures for Li₂, LiO, Li₂O, Li₃O, and Li₂O₂ over the Li₂O samples. Some of their results have been plotted in Figure 4.3.1.2

according to the following equations:

$$\log P_{O_2} \text{ (Pa)} = -(17.80 \times 10^3/T) + 10.62 \quad (17)$$

where $T = 1316$ to 1603 (K)

$$\log P_{LiO} \text{ (Pa)} = -(19.85 \times 10^3/T) + 11.21 \quad (18)$$

where $T = 1352$ to 1663 (K)

$$\log P_{Li_2O} \text{ (Pa)} = -(20.60 \times 10^3/T) + 13.40 \quad (19)$$

where $T = 1352$ to 1663 (K)

Several other investigators⁽¹⁰⁻¹³⁾ have determined the partial pressure of Li₂O over Li₂O in a Pt cell, Figure 4.3.1.3, and are in good agreement except

Figure 4.3.1.1 Li Partial Pressure over Li_2O in a Pt Knudsen Cell

Figure 4.3.1.2 Various Partial Pressures over Li_2O in a Pt Knudsen Cell

Figure 4.3.1.3 Li₂O Partial Pressure over Li₂O in a Pt Knudsen Cell

for Berkowitz et al.⁽¹¹⁾ who differed from the neutral conditions with the appearance of H₂O species. Arons et al.⁽¹³⁾ also made some preliminary measurements using controlled quantities of H₂O in the carrier gas stream and found results similar to that of Berkowitz et al.⁽¹¹⁾. They have shown that moisture enhances the volatility of Li₂O within the system.

In addition to vaporization data obtained using Pt cells, Ikeda et al.⁽⁸⁾ measured the pressures obtained using Ni, Nb, Ta, and Mo cells with the subsequent results:

for Ni-cell and T = 1350 - 1500 K

$$\log P_{Li} \text{ (Pa)} = -(17.48 \times 10^3/T) + 11.65 \quad (20)$$

for Nb-cell and T = 1250 - 1375 K

$$\log P_{Li} \text{ (Pa)} = -(22.32 \times 10^3/T) + 16.64 \quad (21)$$

for Ta-cell and T = 1230 - 1450 K

$$\log P_{Li} \text{ (Pa)} = -(19.26 \times 10^3/T) + 13.43 \quad (22)$$

for Mo-cell and T = 1250 - 1375 K

$$\log P_{Li} \text{ (Pa)} = -(19.94 \times 10^3/T) + 14.82 \quad (23)$$

The results, shown in Figure 4.3.1.4, indicate that Ni and Ta are least reactive over the temperature range of the study. The Mo and Nb cells achieved higher P_{Li} at lower temperatures indicative of the amount of strong interaction between the cell and the Li_2O sample. As in most previous experiments, neutral conditions existed with no H_2O species being observed.

Figure 4.3.1.4 Li Partial Pressure over Li_2O in Knudsen Cells of Various Metals

4.3.2 $Li_2O-Al_2O_3$ SYSTEM

4.3.2.1 $\beta-Li_5AlO_4$

Ikeda et al.⁽¹⁴⁾ and Guggi et al.⁽¹⁵⁾ measured the Li partial pressure over β - and molten Li_5AlO_4 using a Pt Knudsen cell with slightly differing results, as seen in Figure 4.3.2.1. Ikeda et al.⁽¹⁴⁾ found for $\beta-Li_5AlO_4$ (solid) and $T = 1262 - 1333$ K,

$$\log P_{Li} \text{ (Pa)} = -(18.64 \times 10^3/T) + 11.19 \quad (24)$$

while Guggi et al.⁽¹⁵⁾ suggested the relationship for $\beta-Li_5AlO_4$ (solid) and $T = 1195 - 1362$ K,

$$\log P_{Li} \text{ (Pa)} = -(17.23 \times 10^3/T) + 10.80 \quad (25)$$

Figure 4.3.2.1 Li Partial Pressure over β -Li₅AlO₄ (s,l) in a Pt Knudsen Cell

No explanation was apparent to account for the differences between the results since the investigators took elaborate steps to insure sample purity and homogeneity, and measurement reproducibility.

4.3.2.2 γ -LiAlO₂

The results of Ikeda et al.⁽¹⁴⁾ for the vaporization pressures over solid γ -LiAlO₂ from a Pt Knudsen cell are shown in Figure 4.3.2.2 and given below:

for T = 1480 - 1723 K (not shown on Figure 4.3.2.2)

$$\log P_{Li} \text{ (Pa)} = -(20.23 \times 10^3/T) + 11.17 \quad (26)$$

for T = 1723 - 1923 K

$$\log P_{Li} \text{ (Pa)} = -(21.45 \times 10^3/T) + 11.86 \quad (27)$$

$$\log P_{O_2} \text{ (Pa)} = -(20.69 \times 10^3/T) + 10.39 \quad (28)$$

for T = 1850 - 1923 (K)

$$\log P_{Li_2O} \text{ (Pa)} = -(23.58 \times 10^3/T) + 10.56 \quad (29)$$

for T = 1640 - 1923 (K)

$$\log P_{LiO} \text{ (Pa)} = -(22.04 \times 10^3/T) + 9.78 \quad (30)$$

Figure 4.3.2.2 Various Partial Pressures over γ -LiAlO₂ in a Pt Knudsen Cell

The data for P_{Li} presented are in good agreement with those of Guggi et al.⁽¹⁵⁾ and at higher temperatures, with those of Hildenbrand⁽¹⁶⁾, but are smaller than those of Popkov and Semonov⁽¹⁷⁾ as illustrated in Figure 4.3.2.3.

Guggi et al.⁽¹⁸⁾ examined the vaporization of γ -LiAlO₂ in Mo and Ta effusion cells in addition to the standard Pt cell. Their results are plotted in Figure 4.3.2.4 and reveal very little difference between using Mo or Ta in contact with γ -LiAlO₂. This was in contrast to the noticeable difference found when Li₂O was used (see Figure 4.3.1.4). There, Ta resulted in much less Li vaporization than Mo over similar temperatures. As expected, γ -LiAlO₂ in a Pt cell resulted in lower P_{Li} . The results are:

for Mo cell and $T = 1250 - 1430$ K

$$\log P_{Li} \text{ (Pa)} = -(20.37 \times 10^3/T) + 12.75 \quad (31)$$

for Ta cell and $T = 1330 - 1480$ K

$$\log P_{Li} \text{ (Pa)} = -(17.02 \times 10^3/T) + 10.35 \quad (32)$$

Figure 4.3.2.3 Li Partial Pressures over $\gamma\text{-LiAlO}_2$ in a Pt Knudsen Cell

Figure 4.3.2.4 Li Partial Pressures over $\gamma\text{-LiAlO}_2$ in Knudsen Cells of Various Metals

4.3.2.3 LiAl_5O_8

Ikeda et al.⁽¹⁴⁾ measured the partial pressures of Li and LiO over LiAl_5O_8 and found P_{Li} to be slightly higher than an extrapolation of data by Guggi et al.⁽¹⁵⁾. Their results are plotted in Figure 4.3.2.5 and given below:

for $T = 1493 - 1770 \text{ K}$ (Ikeda et al.)

$$\log P_{\text{Li}} (\text{Pa}) = -(21.17 \times 10^3/T) + 11.49 \quad (33)$$

for $T = 1330 - 1570 \text{ (K)}$ (Guggi et al.)

$$\log P_{\text{Li}} (\text{Pa}) = -(9.92 \times 10^3/T) + 4.19 \quad (34)$$

for $T = 1580 - 1750 \text{ (K)}$

$$\log P_{\text{LiO}} (\text{Pa}) = -(25.32 \times 10^3/T) + 11.20 \quad (35)$$

4.3.3 $\text{Li}_2\text{O-SiO}_2$

4.3.3.1 Li_4SiO_4

No data was found.

Figure 4.3.2.5 Partial Pressures over LiAl_5O_8 in a Pt Knudsen Cell

4.3.3.2 Li_2SiO_3

Nakagawa et al.⁽¹⁹⁾ have studied the vaporization of Li_2SiO_3 (s/l) using a Pt Knudsen cell over a temperature range of 1166-1762 K. The determined partial pressures of Li(g), LiO(g), and Li_2O (g) over Li_2SiO_3 (s/l) are listed below and depicted in Figure 4.3.3.1:

for Li_2SiO_3 - solid and $T = 1166 - 1461$ (K)

$$\log P_{\text{Li}} (\text{Pa}) = -(16.98 \times 10^3/T) + 9.63 \quad (36)$$

for Li_2SiO_3 - liquid and $T = 1479 - 1762$ (K)

$$\log P_{\text{Li}} (\text{Pa}) = -(16.04 \times 10^3/T) + 9.10 \quad (37)$$

$$T = 1601 - 1762 \text{ (K)}$$

$$\log P_{\text{LiO}} (\text{Pa}) = -(23.22 \times 10^3/T) + 10.06 \quad (38)$$

$$T = 1527 - 1762 \text{ (K)}$$

$$\log P_{\text{Li}_2\text{O}} (\text{Pa}) = -(17.49 \times 10^3/T) + 6.99 \quad (39)$$

Other partial pressures of SiO and Li_2SiO_3 were seen between 1527 and 1762 K but they were less than LiO and not depicted in Figure 4.3.3.1.

13-6265
7-15-83

Figure 4.3.3.1 Partial Pressures over Li_2SiO_3 in a Pt Knudsen Cell

4.3.4 Li₂O-TiO₂

No data have been found regarding the vaporization pressures of Li₄TiO₄ or Li₂TiO₃.

4.3.5 Li₂O-ZrO₂

4.3.5.1 Li₈ZrO₆

Neubert and Guggi⁽²⁰⁾ calculated the pressure of Li above Li₈ZrO₆ using a Pt Knudsen cell and calculated a relationship for T = 1302 - 1604 (K):

$$\log P_{\text{Li}} (\text{Pa}) = -(17.94 \times 10^3/T) + 11.07 \quad (40)$$

They stated that the vapor phase above the Li₈ZrO₆ consisted mainly of Li and O₂ with the vapor pressure of Li₂O amounting to $\approx 10\%$ of Li. LiO, Li₂ and O were species "seen" in very small quantities. Their results have been displayed in Figure 4.3.5.1.

13-6269
7-15-83

Figure 4.3.5.1 Li Partial Pressures over the Li₂O-ZrO₂ System in Pt Knudsen Cells

4.3.5.2 Li_4ZrO_4

Neubert and Guggi⁽²⁰⁾ measured the vapor pressure of Li above Li_4ZrO_4 and calculated the least-squares relationship below for $T = 1316 - 1611$ (K):

$$\log P_{\text{Li}} \text{ (Pa)} = -(18.21 \times 10^3/T) + 11.13 \quad (41)$$

As with the Li_8ZrO_6 , they noticed small amounts of Li_2O , LiO , Li_2 and O but no quantities were reported. The results have been included in Figure 4.3.5.1.

4.3.5.3 Li_2ZrO_3

Neubert and Guggi⁽²⁰⁾ measured the vapor pressure of Li above solid Li_2ZrO_3 and saw the relationship for $T = 1332 - 1642$ (K):

$$\log P_{\text{Li}} \text{ (Pa)} = -(18.39 \times 10^3/T) + 10.59 \quad (42)$$

Figure 4.3.5.1 contains the data and, as expected, the Li_2ZrO_3 sample resulted in less volatility when compared to Li_8ZrO_6 and Li_4ZrO_4 for a Pt cell.

4.3.6 Li_2O - METAL OXIDE SYSTEMS

A comparison of the P_{Li} exerted in a Pt cell among the solid breeder materials (Li_2O , Li_8ZrO_6 , $\beta\text{-Li}_5\text{AlO}_4$, Li_2SiO_3 , Li_2ZrO_3 and $\gamma\text{-LiAlO}_2$) has been made in Figure 4.3.6.1. Li_2O has the highest values, as expected, followed by Li_8ZrO_6 and $\beta\text{-Li}_5\text{AlO}_4$ and then, $\gamma\text{-LiAlO}_2$, with the lowest Li atom density, has the lowest P_{Li} measured.

In compatibility experiments featuring Li_2O pellets in contact with Mo alloys or with Fe-Ni-Cr alloys, certain corrosion products have appeared, namely Li_4MoO_5 , Li_5FeO_4 and LiCrO_2 . These compounds and their vaporization trends have been studied by several investigators⁽²¹⁻²³⁾, and their findings are displayed in Figure 4.3.6.2. Ikeda et al.⁽²¹⁾ obtained vaporization data on both liquid Li_2MoO_4 and $\beta\text{-Li}_4\text{MoO}_5$ with a Pt Knudsen cell. The results were:

Liquid Li_2MoO_4 for $T = 1160 - 1400$ (K)

$$\log P_{\text{Li}} \text{ (Pa)} = -(17.71 \times 10^3/T) + 10.18 \quad (43)$$

$\beta\text{-Li}_5\text{MoO}_4$ for $T = 1150 - 1445$ (K)

$$\log P_{\text{Li}} \text{ (Pa)} = -(18.70 \times 10^3/T) + 11.04 \quad (44)$$

**Figure 4.3.6.1 Li Partial Pressure over Solid Breeder Candidates
in Pt Knudsen Cells**

**Figure 4.3.6.2 Li Partial Pressure Over Corrosion Products Found During
Li₂O/Metal Compatibility Experiments (Measurements were
made in a Pt Knudsen Cell)**

Much less lithium vaporization was noticed with Li_2MoO_4 and $\beta\text{-Li}_5\text{MoO}_4$ as compared to Li_2O in contact with a Mo Knudsen cell. Thus, even though Li_2MoO_4 and $\beta\text{-Li}_5\text{MoO}_4$ have only been found as corrosion products of Li_2O in contact with Mo or a Mo alloy, they are not the total contribution to the P_{Li} in the temperature region.

Li_5FeO_4 and LiCrO_2 have been the two primary corrosion products found in $\text{Li}_2\text{O}/\text{Fe-Ni-Cr}$ alloy compatibility couples. Takeshita et al.⁽²²⁾ examined the vaporization of Li_5FeO_4 with a Pt Knudsen cell and calculated the relationship:

$$\begin{aligned} &\text{for } T = 1410 - 1490 \text{ (K)} \\ &\log P_{\text{Li}} \text{ (Pa)} = -(17.40 \times 10^3/T) + 10.72 \end{aligned} \quad (45)$$

Li and O_2 were the predominant species observed along with a small quantity of LiO and Li_2O . Omichi et al.⁽²³⁾ measured the vapor pressure over LiCrO_2 using a mass spectrometer associated with a Pt Knudsen cell with the following result:

$$\begin{aligned} &\text{for } T = 1673 - 1873 \text{ (K)} \\ &\log P_{\text{Li}} \text{ (Pa)} = -(22.41 \times 10^3/T) + 11.95 \end{aligned} \quad (46)$$

In addition, the partial pressures of Cr, CrO , and CrO_2 were determined although much less than that of Li.

4.4 THERMAL CONDUCTIVITY

4.4.1 Li-O SYSTEM

Takahashi and Kikuchi⁽²⁴⁾ reported thermal conductivity values for porous Li_2O specimens over a temperature range of $200^\circ\text{--}900^\circ\text{C}$. Their samples ranged from 70.8 to 93.4% theoretical density (TD) for 99% pure Li_2O , with an average crystallite size of $20 \mu\text{m}$ for 79.8% TD and $60 \mu\text{m}$ for 93.4% TD. Their results are illustrated in Figure 4.4.1.1. They measured the material's thermal diffusivity by the laser pulse method under a vacuum environment. The value of the thermal conductivity, k , was then determined from the equation:

Figure 4.4.1.1 Thermal Conductivity of Polycrystalline Li_2O

$$k_n = 4.184 \alpha_n C_p \rho_n \quad (47)$$

where

k_n = thermal conductivity ($\text{W/cm}\cdot\text{K}$)
 α_n = thermal diffusivity (cm^2/sec)
 C_p = specific heat capacity ($\text{cal/g}\cdot\text{K}$)
 ρ_n = bulk density (g/cm^3)

C_p values were taken from the literature,⁽²⁵⁾ and they were obtained by extrapolation above 777 K. The curve is portrayed in Section 4.5 of this report.

Hollenberg⁽²⁶⁾ reported k values for a 84.6% TD Li_2O sample with an average grain size of $6 \mu\text{m}$. His values, taken in a He environment, are plotted in Figure 4.4.1.1 and show a similar trend to the values taken in a vacuum environment with much larger grain sizes. The decrease in thermal conductivity with increasing temperature is consistent with the phonon conduction mechanism. At low temperatures, the mean free path of a phonon is equal to several unit cell lengths and is only slightly affected by defects. At high temperatures, however, the phonon's mean free path approaches unit cell dimensions and is greater influenced by thermal defects.

4.4.2 Li₂O-Al₂O₃ SYSTEM

Gurwell⁽²⁷⁾ presented a thermal conductivity curve for a mixed LiAlO₂ (50 to 75% γ-LiAlO₂ and 25 to 50% α-LiAlO₂) body at temperatures up to 1200 K. The density was listed as 88.5% of 2.62 g/cm³ (ρ of a mixture of α and γ-LiAlO₂) but there is no mention of test procedure, environment or grain size of the sample. The data have been presented in Figure 4.1.3.1.

Hollenberg⁽²⁶⁾ measured the thermal conductivity of a high-purity, fine-grained (< 1 μm) γ-LiAlO₂ (83.8% TD) by the laser pulse technique. The sample was coated with a thin layer of gold to provide an electrical conducting surface and to assure opaqueness to the laser beam. A chromel-alumel thermocouple was placed on the back face to measure the temperature rise after the 9 kW laser heated the front face. All measurements were made in He atmosphere to more closely approximate conditions in a tritium breeding blanket. The system's accuracy was established to be within 5% by measurements made on 316 SS. His findings have also been shown in Figure 4.4.2.1, and although fairly different @ RT, the difference decreases by the time T = 500°C and the curves converge readily at higher temperatures.

Their results:

$$\begin{array}{ll} \text{for } T = 100^\circ - 827^\circ\text{C} & \text{(Gurwell's)} \\ k \text{ (W/m}^\circ\text{-C)} = 3.59 - 6.85 \times 10^{-3} T + 1.02 \times 10^{-5} T^2 & (48) \end{array}$$

$$\begin{array}{ll} \text{for } T = 100^\circ - 600^\circ\text{C} & \text{(Hollenberg's)} \\ k \text{ (W/m}^\circ\text{-C)} = 5.75 - 1.79 \times 10^{-2} T + 3.41 \times 10^{-5} T^2 & (49) \end{array}$$

4.4.3 Li₂O-SiO₂ SYSTEM

Hollenberg⁽²⁶⁾ followed the same procedure discussed in the previous section while investigating Li₄SiO₄. His data, presented in Figure 4.4.3.1, again showed a relatively low, k_n, for Li₄SiO₄ although one higher than that of the γ-LiAlO₂ sample.

Figure 4.4.2.1 Thermal Conductivity of Polycrystalline γ -LiAlO₂ (Hollenberg's Data Was Taken in a He Environment While Gurwell's Was Not Stated)

Figure 4.4.3.1 Thermal Conductivity of Polycrystalline Li₄SiO₄ in a He Environment

The equation for $T = 50^{\circ} - 500^{\circ}\text{C}$ is:

$$k \text{ (W/m-}^{\circ}\text{C)} = 5.19 - 1.23 \times 10^{-2} T + 1.81 \times 10^{-5} T^2 \quad (50)$$

His sample was 85% TD with a grains size of $2 \mu\text{m}$ and the data was generated under a He environment.

4.4.4 Li₂O-TiO₂ SYSTEM

Finn and her coworkers⁽²⁸⁾ examined the thermal conductivity of Li_2TiO_3 (81.4% TD) using the laser pulse technique under a vacuum environment. Their data has been illustrated in Figure 4.4.1 and reveal very little temperature response over $200^{\circ} - 1000^{\circ}\text{C}$ range. The sample was cold pressed at 0.4 GPa and sintered @ 1693 K for 4 hours in vacuum. The final average crystallite (grain) size was $110 \mu\text{m}$ with connected pores at least $50 \mu\text{m}$ in size. Also noticed was the presence of a glassy phase and a closed porosity of 2%. The sample was coated with carbon to insure uniform absorption and preheated to 800°C in vacuum prior to test.

The equation that describes the curve for $T = 100^{\circ} - 1000^{\circ}\text{C}$ is:

$$k \text{ (W/m-}^{\circ}\text{C)} = 1.885 - 8.28 \times 10^{-4} T + 3.69 \times 10^{-7} T^2 \quad (51)$$

4.4.5 Li₂O-ZrO₂ SYSTEM

Hollenberg⁽³⁾ followed the same procedure outlined in section 4.4.2 to determine the thermal conductivity of Li_2ZrO_3 samples by the laser pulse method under He atmosphere. One sample was cold pressed and sintered to 78.9% TD in a He atmosphere while the other was hot pressed to 85% TD with a average grain size of $2 \mu\text{m}$. Grain size and pore size were not reported but the data have been depicted in Figure 4.4.5.1.

Finn, et al.⁽⁴⁾ determined the thermal diffusivity of Li_2ZrO_3 and plotted its thermal conductivity in Figure 4.4.5.1. The measurements were made in vacuum and can be compared to those made in He with a factor of 2 difference. Significant microcracking was observed which in part is responsible for the low thermal conductivity. In addition, a hysteresis effect was seen which could be the result of a crack healing process or of glassy phase formation.

Figure 4.4.4.1 Thermal Conductivity of Polycrystalline Li_2TiO_3 in a Vacuum Environment

Figure 4.4.5.1 Thermal Conductivity of Polycrystalline Li_2ZrO_3 Bodies

The equations that describe the results are:

$$78.9\% \text{ TD} - (\text{He}) - T = 100^{\circ} - 400^{\circ}\text{C}$$

$$k \text{ (W/m-}^{\circ}\text{C)} = 2.86 - 1.63 \times 10^{-2} T + 7.42 \times 10^{-5} T^2 \quad (52)$$

$$86.\% \text{ TD} - (\text{He}) - T = 100^{\circ} - 500^{\circ}\text{C}$$

$$k \text{ (W/m-}^{\circ}\text{C)} = 2.32 - 5.41 T + 2.00 T^2 \quad (53)$$

$$88\% \text{ TD} - (\text{Vacuum}) - T = 100^{\circ} - 800^{\circ}\text{C}$$

$$k \text{ (W/m-}^{\circ}\text{C)} = 4.65 \times 10^{-1} + 1.87 \times 10^{-4} T - 3.79 \times 10^{-7} T^2 \quad (54)$$

4.4.6 Li₂O - METAL OXIDE SYSTEMS

A comparison of the thermal conductivity values for the various solid breeder candidates has been made in Figure 4.4.6.1. The data for the majority was generated in a blanket-like He environment except for Li₂TiO₃. At lower temperatures, Li₂O has much higher values but at higher temperatures (> 500°C)

Figure 4.4.6.1 Comparison of Thermal Conductivity Values for Various Solid Breeder Candidates

the differences narrow if the curves were extrapolated. An interesting trend is the slightly increasing values for Li_2TiO_3 in a vacuum appears to have very little change although another slightly upward trend is noticed. If evaluated in a He environment, Li_2TiO_3 would probably be two to three times higher, similar to the relationship "seen" for Li_2ZrO_3 .

4.5 SPECIFIC HEAT

4.5.1 Li-O SYSTEM

The specific heat of Li_2O has been studied by several investigators. Johnston and Bauer⁽²⁹⁾ produced Li_2O from the decomposition reaction of LiOH in a reducing atmosphere and further heated the Li_2O in a Ni boat until it was 99.9% pure. They used the drop calorimetry method and determined the heat capacity from 16 to 304 K. Their equation was

$$C_p \text{ (cal/mol)} = -0.501 - 0.02167 T + 0.37356 (1000/T)^3 \quad (55)$$

More useful data have been gathered by Tanifuji et al.,⁽³⁰⁾ Barin and Knacke⁽³¹⁾, Shomate and Cohen,⁽²⁵⁾ and Rodigina and Gomelskii⁽³²⁾ for Li_2O . Tanifuji performed the latest work, which was in excellent agreement with the others. The work of Tanifuji et al., was done with an adiabatic scanning calorimeter, whereas the others chose the drop calorimetry technique. The data are in such good agreement that only Tanifuji's values has been plotted on Figure 4.5.1.1. His equation was

$$C_p \text{ (J/kg-K)} = 2.518 \times 10^3 + 0.333 T - 8.382 \times 10^7 T^{-2} \quad (56)$$

for a temperature range of 306-1073 K.

4.5.2 $\text{Li}_2\text{O-Al}_2\text{O}_3$ SYSTEM

Hollenberg⁽²⁶⁾ and Christensen et al.,⁽³³⁾ have made measurements on LiAlO_2 over the temperature range of interest. Both results are plotted in Figure

Figure 4.5.1.1 Specific Heat of Li_2O

4.5.2.1 with Hollenberg's being slightly lower ($\approx 10\%$) than Christensen's values. Hollenberg measured a pure $\gamma\text{-LiAlO}_2$ sample with a Hewlett-Packard DSC-II scanning calorimeter using a sapphire standard. Christensen used the drop calorimetry method for his measurements and may have had a mixed phase of LiAlO_2 for his sample. This might account for his slightly higher measurements. Christensen's equations was:

$$C_p \text{ (J/kg-K)} = 0.335 + 4.39 \times 10^{-5} T - 9.10 \times 10^3 T^{-2} \quad (57)$$

for a temperature in the 298-1800 K range. Hollenberg's was

$$C_p \text{ (J/kg-K)} = 1.047 \times 10^3 + 0.402 T - 1.800 \times 10^7 T^{-2} \quad (58)$$

which covered a range of 398-700 K.

4.5.3 $\text{Li}_2\text{O-SiO}_2$ SYSTEM

Hollenberg⁽²⁶⁾ and Bennington et al.⁽³⁴⁾ have determined the specific heat for various lithium silicates. In Hollenberg's experiment, the Li_4SiO_4

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Figure 4.5.2.1 Specific Heat of γ -LiAlO₂

sample had a phase impurity of Li₂SiO₃ (1-t wt.%), while Bennington's samples of Li₂SiO₃ and Li₂Si₂O₅ were reported to be phase pure. Hollenberg's technique has been described in Section 4.5.2, and his equation for the specific heat of Li₄SiO₄ was:

$$C_p \text{ (J/kg-K)} = 9.399 \times 10^2 + 1.458 T + 4.011 \times 10^6 T^{-2} \quad (59)$$

from 373-773 K and has been illustrated in Figure 4.5.3.1.

Bennington and his coworkers⁽³⁴⁾ employed the drop calorimetry method in determining the C_p values of both Li₂SiO₃ and Li₂Si₂O₅. Their results are plotted in Figure 4.5.3.1. Their equations are:

$$C_p \text{ (kJ/kg-°C)} = 1.069 + 2.417 \times 10^{-3} T - 3.641 \times 10^{-6} T^2 \quad (60)$$

for Li₂SiO₃ from 25-325°C, and

$$C_p \text{ (kJ/kg-°C)} = 9.16 \times 10^{-1} + 2.172 \times 10^{-3} T - 3.118 \times 10^{-6} T^2 \quad (61)$$

for Li₂Si₂O₅ from 25-825°C

Figure 4.5.3.1 Specific Heat of Compounds in the Li₂O-SiO₂ System

4.5.4 Li₂O-TiO₂ SYSTEM

Christensen, et.al.,⁽³³⁾ reported the values plotted in Figure 4.5.4.1 for Li₂TiO₃. A $\alpha \rightarrow \beta$ phase transition was seen in this system but it occurred @ 1485 K, a temperature well above the normal range of a breeding blanket. They used the drop calorimetry method and covered the temperature range 25°-900°C. Their equation was:

$$C_p \text{ (kJ/kg-}^\circ\text{C)} = 9.732 \times 10^{-1} + 1.599 \times 10^{-3} T - 2.25 \times 10^{-6} T^2 \quad (62)$$

Figure 4.5.4.1 Specific Heat of Li_2TiO_3

4.5.5 $\text{Li}_2\text{O-ZrO}_2$ SYSTEM

Barin and Knacke⁽³¹⁾ and Hollenberg⁽²⁶⁾ both reported C_p values for monoclinic Li_2ZrO_3 . Hollenberg used a phase pure material and a scanning DSC-II calorimeter to achieve almost identical values to those theoretically predicted by Barin. Hollenberg's equation was

$$C_p (\text{J/kg-K}) = 7.494 \times 10^2 + 0.312 T \quad (63)$$

from 373-773 K. The plot on Figure 4.5.5.1 utilizes Hollenberg's and Barin's data to extend the curve to 400°C. The curve is smooth, indicating no phase transitions; this finding is in agreement with other investigators who report the monoclinic - tetragonal phase change occurring @ 1100°C or 1373 K.

Figure 4.5.5.1 Specific Heat of Li_2ZrO_3

4.6 THERMAL EXPANSION

4.6.1 Li-O System

Hollenberg⁽²⁶⁾ measured the thermal expansion of a Li_2O pellet with a Theta Dilatronic dilatometer in an inert atmosphere using a platinum standard for calibration. Several runs were made to insure that sintering, hysteresis, or swelling had not occurred and affected the results. The pellet was produced by hot pressing to 85% TD with an average crystallite size of 6 μm . His results have been illustrated in Figure 4.6.1.1 with the major portion of the curve being expressed as

$$\text{LTE (\%)} = -5.707 \times 10^{-4} + 2.081 \times 10^{-3}T + 8.388 \times 10^{-7} T^2 \quad (64)$$

over a temperature range of 100°C to 1000°C.

Kurasawa et.al.⁽³⁵⁾ examined the linear thermal expansion of a single crystal of Li_2O prepared by the floating zone growth method using an infrared imaging

furnace. Their results have been depicted in Figure 4.6.1.1 and are very close to the data of Hollenberg's 85% TD polycrystalline sample.

$$\text{LTE (\%)} = 8.417 \times 10^{-4} + 1.26 \times 10^{-3} T + 2.72.6 \times 10^{-6} T^2 \quad (64)$$

This was consistent with the findings of little variation for sintered pellets of Li_2O with densities ranging from 75.5 to 92.5% TD except at temperatures above 800°C .

Figure 4.6.1.1 Linear Thermal Expansion of Single Crystal and Polycrystalline Li_2O

4.6.2 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM

Hollenberg⁽²⁶⁾ and Hummel⁽³⁶⁾ have both measured the thermal expansion of $\gamma\text{-LiAlO}_2$ samples. Hummel prepared his $\gamma\text{-LiAlO}_2$ by solid state reaction @ 1500°C for 7 to 15 hours. No mention was made of firing atmosphere but it was presumed to be air. After grinding, the $\gamma\text{-LiAlO}_2$ was pressed with a binder and refired at 1500°C for 1 hour. At the time he presented his data, there were no previous works for comparison or verification. Consequently he believed his x-ray analysis to be that of pure $\gamma\text{-LiAlO}_2$. However, his data

contained three d-spacings, which have been shown not to be present in phase pure γ -LiAlO₂. They are at 3.52, 2.79 and 1.52 Å. These peaks indicate the presence of a second phase, possibly LiAl₅O₈, due to Li₂O volatilization at high temperatures.

Hollenberg hot-pressed a sample of γ -LiAlO₂ and verified its phase purity against the JCPDS X-ray Diffraction Card File. His sample was made to 85% TD with an average grain size of < 1 μm. His data were obtained with a Theta Dilometer and closely matched the values presented by Hummel. Thus the data, in Figure 4.6.2.1, can be described using one equation:

$$\text{LTE} (\%) = 3.750 \times 10^{-4} + 9.604 \times 10^{-4} T + 2.480 \times 10^{-7} T^2 \quad (66)$$

being useful from 100° to 900°C for γ -LiAlO₂.

In addition, Hummel⁽³⁶⁾ measured the thermal expansion of LiAl₅O₈ and found

$$\% \text{ LTE} (\%) = -4.883 \times 10^{-2} + 8.443 \times 10^{-4} T - 2.937 \times 10^{-7} T^2 \quad (67)$$

from T = 100° to 900°C.

Figure 4.6.2.1 Linear Thermal Expansion Polycrystalline γ -LiAlO₂ and LiAl₅O₈.

4.6.3 Li₂O-SiO₂ SYSTEM

Soga⁽³⁷⁾ first reported the thermal expansion of Li₄SiO₄ from 25° to 400°C. He pressed and sintered his sample @ 1100°C for 3 hours and then used a Brinkman-Netzsch dilatometer for his measurements. No mention of final phase purity, chemistry or crystallite size was made. His data, was presented as

$$\text{LTE (\%)} = 2.04 \times 10^{-3} T \quad (68)$$

from 25° to 400° C. These data are not too much different from Hollenberg's data for the same temperature range. Hollenberg used a Theta Dilatometer with a Pt standard on a Li₄SiO₄ (85% TD) sample which had an average grain size of 2 μm. His full range of data have been presented in Figure 4.6.3.1 with the relationship between 80° and 900°C being expressed as

$$\text{LTE (\%)} = -4.786 \times 10^{-4} + 1.881 \times 10^{-3}T + 8.334 \times 10^{-7}T^2 \quad (69)$$

Kirchner et al.⁽³⁸⁾ reported the linear thermal expansion of Li₂SiO₃ and Li₂Si₂O₅ with the following results:

Li₂SiO₃ for T = 100° to 700°C

$$\text{LTE (\%)} = -1.124 \times 10^{-2} + 1.129 \times 10^{-3}T \quad (70)$$

Li₂Si₂O₅ for T = 100° to 700°C

$$\text{LTE (\%)} = -2.943 \times 10^{-2} + 7.196 \times 10^{-4}T + 5.689 \times 10^{-7}T^2 \quad (71)$$

Figure 4.6.3.1 Linear Thermal Expansion of Compounds in the $\text{Li}_2\text{O-SiO}_2$ System

4.6.4 Li₂O-TiO₂ SYSTEM

Girard and his co-workers⁽³⁹⁾ examined a Li₂TiO₃ body formulated to a high density with very little porosity. They were trying to duplicate the high density ($\approx 90\%$) achieved by plasma-spraying a coating of Li₂TiO₃ onto a metal surface. No further details were given as to the exact material density or purity or even test method. Their results have been plotted in Figure 4.6.4.1 with the following equation describing their results.

$$\text{LTE (\%)} = -5.573 \times 10^{-2} + 1.455 \times 10^{-3}T + 5.505 \times 10^{-7}T^2 \quad (72)$$

for $T = 100^\circ$ to 800°C

Figure 4.6.4.1 Linear Thermal Expansion of Polycrystalline Li₂TiO₃

4.6.5 Li₂O-ZrO₂ SYSTEM

Hollenberg⁽²⁶⁾ used a Theta Dilatometer with a Pt standard to measure the thermal expansion of Li₂ZrO₃. The hot pressed sample was 85% TD with an average grain size of 2 μm . He verified it as being single phase by x-ray

diffraction and chemical analysis, which revealed < 2000 μg /total metallic impurities. His curve has been reproduced in Figure 4.6.5.1 with

$$\text{LTE } (\%) = -4.293 \times 10^{-4} + 9.917 \times 10^{-4}T \quad (73)$$

being valid from 100° to 900°C.

Figure 4.6.5.1 Linear Thermal Expansion of Polycrystalline Li_2ZrO_3

4.6.6 Li_2O - METAL OXIDE SYSTEMS

A comparison of LTE (%) of the various materials has been illustrated in Figure 4.6.6.1 with Li_2O and Li_4SiO_4 showing the highest values. Li_2TiO_3 appears to be in the middle ground with $\gamma\text{-LiAlO}_2$, Li_2SiO_3 , and Li_2ZrO_3 being closely bunched.

Figure 4.6.6.1 Comparison of Linear Thermal Expansion of
Solid Breeder Candidates

4.7 MISCELLANEOUS

4.7.1 Li₂O

$$\Delta H_f^\circ, 298.15 \text{ K} = -142.57 \text{ kcal/mole} \quad (\text{Ref. 29})$$

$$\Delta H_m = 14 \text{ kcal/mole} \quad (\text{Ref. 40})$$

$$S_{298.15 \text{ K}}^\circ = 9.056 \text{ cal/deg-mole} \quad (\text{Ref. 40})$$

$$S_T^\circ - S_{298.15 \text{ K}}^\circ = (\text{cal/mole-K}) = -1.538 \times 10^1 + 6.157 \times 10^{-2}T - 3.680 \times 10^{-5}T^2 + 1.107 \times 10^{-8}T^3 \quad (74)$$

$$\text{for } T = 300 - 1400 \text{ K} \quad (\text{Ref. 30})$$

$$H_T^\circ - H_{298.15 \text{ K}}^\circ (\text{cal/mole}) = -3.124 \times 10^3 + 7.467 T + 1.091 \times 10^{-2}T^2 - 2.819 \times 10^{-6}T^3 \quad (75)$$

$$\text{for } T = 300-1400 \text{ K} \quad (\text{Ref. 30})$$

$$- (G_T^\circ - H_{298.15 K}^\circ)/T \text{ (cal/mole - K)} = 8.389 - 4.443 \times 10^{-3} T + 2.180 \times 10^{-5} T^2 - 8.488 \times 10^{-9} T^3 \quad (76)$$

for T = 300 - 1400 K

4.7.2 Li₂O-Al₂O₃ SYSTEM

4.7.2.1 β -Li₅AlO₄

$$\Delta H_f^\circ, 298.15 \text{ K} = -4 \text{ kcal/mole} \quad (\text{Ref. 15})$$

4.7.2.2 γ -LiAlO₂

$$\Delta H_f^\circ, 298.15 \text{ K} = 284 \text{ kcal/mole} \quad (\text{Ref. 40,41})$$

$$\Delta H_m = 21 \text{ kcal/mole} \quad (\text{Ref. 40})$$

$$S_{298.15}^\circ = 12.75 \text{ cal/deg-mole} \quad (\text{Ref. 40})$$

$$S_T^\circ - S_{298.15 K}^\circ \text{ (cal/mole-K)} = -1.972 \times 10^1 + 7.836 \times 10^{-2} T - 4.445 \times 10^{-5} T^2 + 1.143 \times 10^{-8} T^3 \quad (77)$$

for T = 300 - 1400 K (Ref. 40)

$$H_T^\circ - H_{298.15 K}^\circ \text{ (kcal/mole)} = -4.161 + 1.028 \times 10^{-2} T + 1.358 \times 10^{-5} T^2 + 4.219 \times 10^{-9} T^3 \quad (78)$$

for T = 300 - 1400 K (Ref. 40)

$$- (G_T^\circ - H_{298.15 K}^\circ)/T \text{ (cal/mole-K)} = 1.159 \times 10^1 - 2.789 \times 10^{-3} T + 2.342 \times 10^{-5} T^2 - 9.165 \times 10^{-9} T^3 \quad (79)$$

(Ref. 40)

4.7.2.3 LiAl₅O₈

$$\Delta H_f^\circ, 298.15 \text{ K} = -40 \text{ kcal/mole} \quad (\text{Ref. 15})$$

4.7.3 Li₂O-SiO₂ SYSTEM

4.7.3.1 Li₄SiO₄

$$\Delta H_f^\circ, 298.15 \text{ K} = -536 \text{ kcal/mole} \quad (\text{Ref. 42})$$

$$S_{298.15 \text{ K}}^\circ = 4.8 \text{ cal/deg-mole} \quad (\text{Ref. 42})$$

4.7.3.2 Li₂SiO₃

$$\Delta H_f^\circ, 298.15 \text{ K} = -394 \text{ kcal/mole} \quad (\text{Ref. 34,40})$$

$$\Delta H_m^\circ = 6.7 \text{ kcal/mole} \quad (\text{Ref. 40})$$

$$S_{298.15 \text{ K}}^\circ = 19 \text{ cal/deg-mole} \quad (\text{Ref. 34,40})$$

$$S_T^\circ - S_{298.15 \text{ K}}^\circ \text{ (cal/K-mole)} = -2.893 \times 10^1 + 1.149 \times 10^{-1} T - 6.501 \times 10^{-5} T^2 + 1.750 \times 10^{-8} T^3 \quad (80)$$

$$\text{for } T = 300 - 1250 \text{ K} \quad (\text{Ref. 40})$$

$$H_T^\circ - H_{298.15 \text{ K}}^\circ \text{ (kcal/mole)} = -5.768 + 1.301 \times 10^{-2} T + 2.339 \times 10^{-5} T^2 - 7.293 \times 10^{-9} T^3 \quad (81)$$

$$\text{for } T = 300 - 1250 \text{ K}$$

$$- (G_T^\circ - H_{298.15 \text{ K}}^\circ)/T \text{ (cal/mole-K)} = 1.868 \times 10^1 - 1.108 \times 10^{-2} T + 4.543 \times 10^{-5} T^2 - 1.850 \times 10^{-8} T^3 \quad (82)$$

$$\text{for } T = 300 - 1250 \text{ K} \quad (\text{Ref. 40})$$

4.7.3.3 Li₂Si₂O₅

$$\Delta H_f^\circ, 298.15 \text{ K} = -612 \text{ kcal/mole} \quad (\text{Ref. 34})$$

$$S_{298.15 \text{ K}}^\circ = 29.20 \text{ cal/deg-mole} \quad (\text{Ref. 34})$$

$$S_T^\circ - S_{298.15\text{ K}}^\circ \text{ (cal/mole-K)} = -4.144 \times 10^1 + 1.638 \times 10^{-1} T \\ - 9.058 \times 10^{-5} T^2 + 2.420 \times 10^{-8} T^3 \quad (83)$$

for $T = 300 - 1250\text{ K}$ (Ref. 40)

$$H_T^\circ - H_{298.15\text{ K}}^\circ \text{ (kcal/mole)} = -8.191 + 1.802 \times 10^{-2} T \\ + 3.479 \times 10^{-5} T^2 - 1.051 \times 10^{-8} T^3 \quad (84)$$

for $T = 300 - 1250\text{ K}$ (Ref. 40)

$$- (G_T^\circ - H_{298.15\text{ K}}^\circ) / T \text{ (cal/mole-K)} = 2.870 \times 10^1 \\ - 1.641 \times 10^{-2} T + 6.616 \times 10^{-5} T^2 \\ - 2.682 \times 10^{-8} T^3 \quad (85)$$

for $T = 300 - 1250\text{ K}$ (Ref. 40)

4.7.4 Li₂O-TiO₂ SYSTEM

4.7.4.1 Li₂TiO₃

$$\Delta H_f^\circ, 298.15\text{ K} = -399.3 \text{ kcal/mole} \quad (\text{Ref. 40})$$

$$\Delta H_m = 26 \text{ kcal/mole} \quad (\text{Ref. 40})$$

$$\Delta S_{298.15\text{ K}}^\circ = 22 \text{ cal/deg mole} \quad (\text{Ref. 43})$$

$$S_T^\circ - S_{298.15\text{ K}}^\circ \text{ (cal/mole-K)} = -3.163 \times 10^1 + 1.272 \times 10^{-1} T \\ - 7.670 \times 10^{-5} T^2 + 2.052 \times 10^{-8} T^3 \quad (86)$$

for $T = 300 - 1400\text{ K}$ (Ref. 40)

$$H_T^\circ - H_{298.15\text{ K}}^\circ \text{ (kcal/mole)} = -6.919 + 1.842 \times 10^{-2} T \\ + 1.769 \times 10^{-5} T^2 - 5.518 \times 10^{-9} T^3 \quad (87)$$

for $T = 300 - 1400\text{ K}$ (Ref. 33)

$$- (G_T^\circ - H_{298.15\text{ K}}^\circ) / T \text{ (cal/mole-K)} = 1.983 \times 10^1 - 2.874 \times 10^{-3} T \\ + 3.468 \times 10^{-5} T^2 - 1.371 \times 10^{-8} T^3 \quad (88)$$

for $T = 300 - 1400\text{ K}$ (Ref. 40)

4.7.5 Li₂O-ZrO₂ SYSTEM

4.7.5.1 Li₈ZrO₆

$$H_f^\circ, 298.15 \text{ K} = -852 \text{ kcal/mole} \quad (\text{Ref. 20})$$

4.7.5.2 Li₄ZrO₄

$$H_f^\circ, 298.15 \text{ K} = -565 \text{ kcal/mole} \quad (\text{Ref. 20})$$

4.7.5.3 Li₂ZrO₃

$$\Delta H_f^\circ = -420 \text{ kcal/mole} \quad (\text{Ref. 20})$$

$$S_{298.15 \text{ K}}^\circ = 21.9 \text{ cal/deg-mole} \quad (\text{Ref. 20})$$

$$S_T^\circ - S_{298.15 \text{ K}}^\circ = (\text{cal/mole-K}) = -3.172 \times 10^1 + 1.273 \times 10^{-1} T \\ - 7.616 \times 10^{-5} T^2 + 2.079 \times 10^{-8} T^3 \quad (89)$$

$$\text{for } T = 300 - 1400 \text{ K} \quad (\text{Ref. 20})$$

$$H_T^\circ - H_{298.15 \text{ K}}^\circ = (\text{kcal/mole}) = -6.946 + 1.857 \times 10^{-2} T \\ + 1.727 \times 10^{-5} T^2 - 4.626 \times 10^{-9} T^3 \quad (90)$$

$$\text{for } T = 300 - 1400 \text{ K} \quad (\text{Ref. 20})$$

$$- (G_T^\circ - H_{298.15 \text{ K}}^\circ)/T (\text{cal/mole-K}) = 1.984 \times 10^1 \\ - 3.165 \times 10^{-3} T + 3.523 \times 10^{-5} T^2 - 1.379 \times 10^{-8} T^3 \quad (91)$$

$$\text{for } T = 300 - 1400 \text{ K} \quad (\text{Ref. 20})$$

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5.0 COMPATIBILITY OF LITHIUM CERAMICS AND METALS

5.1 INTRODUCTION

Since solid breeding materials will be in contact with metal structure and coolant tubes during a blanket's operating temperatures, any interactions must be considered. One concern centers on the migration of "active" portions of the solid breeder and/or metal to the interface and its subsequent reaction or scale formation. Depending upon the amount or type of attack, the reaction layer could lead to chemical or stress corrosion and eventual cracking of the metal. In addition, any interaction could result in a two-phase layer within the solid breeder itself which might possess low temperature liquid phases.

5.2 Li-O SYSTEM

Takeshita et al.⁽¹⁾ studied the reaction between an Li_2O 88% TD pellet and Mo or molybdenum-base alloy TZM - (Titanium-Zirconium-Molybdenum) discs. The sample surfaces were initially electrolytically polished so that intimate contact could be assured. Then the reaction couples were stacked in a 316 SS cylinder and heated in a resistance furnace from 800°-1100°C for 100 hours under a dynamic vacuum of 10^{-5} torr. Their results (listed in Figure 5.2.1) indicate very little interaction between Li_2O and Mo (sintered) or Mo (EBM - Electron Beam Melted) below 1000°C and with TZM below 950°C. Very little physical change in either the ceramic or metals was observed below these temperatures. However, at or above these temperatures a black reaction layer was observed on all three metallic samples, and this layer was identified by x-ray diffraction to be $\alpha\text{-Li}_4\text{MoO}_5$. In addition, at the higher temperatures another layer was observed but its pattern did not correspond to any compound known in the Li_2O -Mo system. The authors did not report any changes in the Li_2O samples other than the loss of surface Li_2O required to form Li_4MoO_5 on the metal surface.

Most of the compatibility studies^(2,3,5) have centered on the use of Li_2O with the Fe-Ni-Cr alloys such as 316 stainless steel (SS), Incoloy 800, Hastelloy X-R, Inconel 600, HT-9, a Ni coated 316 SS, and pure Ni. The studies were

FIGURE 5.2.1 LITHIA/METAL COMPATIBILITY RESULTS

REACTION COUPLE	TEMP. °C	TEST CONDITIONS ATMOSPHERE (TORR)	TIME (HRS)	EFFECT ON METAL		EFFECT ON CERAMIC		REF.
				WT. CHANGE (MG/CM ²)	SCALE TH. (μm)	IMPURITY	IMPURITY	
Li ₂ O/ Mo (Sintered)	800	10 ⁻⁵ (dynamic)	100	± 0	-			1
	850	"	"	± 0.1	-			"
	875	"	"	± 0.1	-			"
	900	"	"	± 0	1.2 ± 0.2			"
	950	"	"	- 0.05	3.3 ± 1.1			"
					2.9 ± 0.5			"
	1000	"	"	+ 0.72	9.5 ± 2.3	Li ₄ MoO ₅		"
					8.3 ± 1.7	"		"
	1030	"	25		11.3	"		"
	1030	"	100		16.0	"		"
	1030	"	256		44.5	"		"
	1030	"	500		56.0	"		"
	1050	"	100	+ 1.49	23.4 ± 3.4	"		"
					21.1 ± 7.8	"		"
Li ₂ O/ Mo (EBM)	1100	"	100	+ 3.32	40.3 ± 4.3	"		"
					38.9 ± 6.0	"		"
	800	10 ⁻⁵ (dynamic)	100	± 0	-			1
	850	"	"	+ 0.05	-			"
	875	"	"	+ 0.05	-			"
	900	"	"	0.14	1.0 ± 0.2			"
	950	"	"	- 0.05	3.7 ± 0.6			"
					3.4 ± 0.5			"
	1000	"	"	+ 0.58	7.0 ± 1.7	Li ₄ MoO ₅		"
					6.1 ± 1.2	"		"
	800	10 ⁻⁵ (dynamic)	100	+ 0.05	-			1
	850	"	"	+ 0.10	-			"
	875	"	"	+ 0.10	-			"
	900	"	"	- 0.05	4.1 ± 0.9	Li ₄ MoO ₅		"
Li ₂ O/TZM					3.9 ± 0.9	"		"
	1000	"	"	+ 1.00	11.6 ± 4.2	"		"
					4.9 ± 1.0	"		"
	1050	"	"	+ 4.49	40.3 ± 6.0	"		"
					20.3 ± 6.0	"		"
	1100	"	"	+ 7.88	82.1 ± 13.9	"		"
					59.5 ± 3.0			"

FIGURE 5.2.1 LITHIA/METAL COMPATIBILITY RESULTS
(CONTINUED)

REACTION COUPLE	TEST CONDITIONS			EFFECT ON METAL			EFFECT ON CERAMIC		REF.
	TEMP. °C	ATMOSPHERE (TORR)	TIME (HRS)	WT. CHANGE (MG/CM ²)	SCALE TH. (μm)	IMPURITY	IMPURITY		
Li ₂ O/316 SS	500	2.5 x 10 ² He (Static)	410	0.33	1.48				3
	550	2.5 x 10 ² He (Static)	410	0.59	3.18				3
		7.5 x 10 ² He (Static)	410	3.1	18				5
	600	2.5 x 10 ² He (Static)	410	0.67	4.80				3
				22.4 ± 2.2 (gb)					
	650	2.5 x 10 ² He (Static)	410	1.10	6.71				3
		7.5 x 10 ² He (Static)	1035	3.2	35	LiFeO ₄ , LiCrO ₂			5
	650				28.8 ± 2.7(gb)				
					23.9 ± 4.0(gb)				
	700	2.5 x 10 ² He (Static)	410	1.22					3
	750	2.2 x 10 ² He (Static)	410	1.26	9.22				3
					17.8 ± 2.5(gb)				
					18.1 ± 2.3(gb)				
	800	10 ⁻⁵ (Dynamic)	100	+ 0.05	1.8 ± 0.5	LiCrO ₂	Li ₅ FeO ₄		2
					1.3 ± 0.6	"	"		"
	850	"	"	"	- 0.05	3.8 ± 1.6	"	"	"
					2.5 ± 0.8	"	"		"
	875	"	"	"	+ 0.19	19.1 ± 3.9	"	"	"
					19.1 ± 3.7	"	"		"
	900	"	"	"	+ 0.19	39.5 ± 7.6	"	"	"
					29.4 ± 6.7	"	"		"
	950	"	"	"	+ 1.49	59.1 ± 11.5	"	"	"
					67.6 ± 6.1	"	"		"
	1000	"	"	"	+ 5.87	143 ± 16	"	"	"
					133 ± 8	"	"		"
	1050	"	"	"	+ 9.34	210 ± 12	"	"	"
					195 ± 12	"	"		"
	1100	"	"	"	+14.69	360 ± 21	"	"	"
						373 ± 12	"	"	"
Li ₂ O/316 SS with a 20mil Ni coating	550	7.5 x 10 ² He (Static)	410	0.4	6.0	LiCrO ₂			5
	650	" " "	1035	0.6	10.0				"
Li ₂ O/ Incoloy 800	500	7.5 x 10 ² He (Static)	410	0.39	3.16				3
	550	7.5 x 10 ² He (Static)	410	0.65	6.08				3
					5.7 ± 2.1(gb)				
					9.7 ± 3.0(gb)				
	600	7.5 x 10 ² He (Static)	410	0.68	8.37				3
					12.0 ± 2.1(gb)				
					11.4 ± 2.4(gb)				

FIGURE 5.2.1 LITHIA/METAL COMPATIBILITY RESULTS
(CONTINUED)

REACTION COUPLE	TEMP. °C	TEST CONDITIONS		TIME (HRS)	EFFECT ON METAL		EFFECT ON CERAMIC		REF.
		ATMOSPHERE (TORR)			WT. CHANGE (MG/CM ²)	SCALE TH. (μm)	IMPURITY	IMPURITY	
Li ₂ O/ Hastelloy X-R	1000	10 ⁻⁵	(Dynamic)	100	+ 1.54	38 ± 9	LiCrO ₂	Li ₅ FeO ₄	2
						44 ± 6	"	"	"
	1050	"	"	"	+ 4.82	83 ± 4	"	"	"
						84 ± 5	"	"	"
Li ₂ O/ Inconel 600	1100	"	"	"	+15.21	172 ± 7	"	"	"
						250 ± 15	"	"	"
	500	7.5 x 10 ²	He (Static)	410	0.16	1.03			3
	550	"	"	"	0.22	1.32			
	600	"	"	"	0.45	2.65			
	650	"	"	"	0.62	3.27			
	650	"	"	"		9.8± 0.9(gb)			
						8.9± 0.8(gb)			
	750	"	"	"	0.89	3.30			
	750	"	"	"		21.6± 5.9(gb)			
						18.4± 4.2(gb)			
	800	10 ⁻⁵	(Dynamic)	100	+ 0.25	6.0± 2.7	LiCrO ₂	Li ₄ FeO ₄	2
		"	"	"		6.1± 2.4	"	"	"
		"	"	"		19.5± 6.6(gb)	"	"	"
850		"	"	"	+ 1.37	19.6± 5.7(gb)	"	"	"
		"	"	"		13.1± 3.8	"	"	"
		"	"	"		13.5± 2.7	"	"	"
		"	"	"		44.5± 13.1(gb)	"	"	"
		"	"	"		44.0± 9.9(gb)	"	"	"
	875	"	"	"	+ 2.62	20.9± 2.4	"	"	"
		"	"	"		26.6± 6.8	"	"	"
		"	"	"		49.6± 7.9(gb)	"	"	"
		"	"	"		54.5± 3.3(gb)	"	"	"
	900	"	"	"	+ 2.37	33.8± 5.5			"
950		"	"	"	+ 5.81	21.2± 5.3			"
		"	"	"		56.8± 16.1			"
		"	"	"		122.6± 25.9			"
		"	"	"		89.3± 22.1(gb)			"
1000		"	"	"	+ 7.99	114 ± 9			"
		"	"	"		109 ± 7			"

FIGURE 5.2.1 LITHIA/METAL COMPATIBILITY RESULTS
(CONTINUED)

REACTION COUPLE	TEMP. °C	TEST CONDITIONS ATMOSPHERE (TORR)	TIME (HRS)	WT. CHANGE (MG/CM ²)	SCALE TH. (μm)	IMPURITY	EFFECT ON CERAMIC IMPURITY	REF.
Li ₂ I/ Inconel 600	1050	10 ⁻⁵ (dynamic)	100	+11.11	141 ± 11			2
		" "	"		131 ± 9			"
	1100	" "	"	+19.60	222 ± 15			"
			"		230 ± 18			
Li ₂ O/Ni	800	10 ⁻⁵ (dynamic)	100	- 0.05		None	None	2
	850	" "	"	- 0.05				"
	875	" "	"	- 0.29				"
	900	" "	"	- 0.59				"
	950	" "	"	- 0.87				"
	1000	" "	"	- 0.67				"
	1050	" "	"	- 0.48				"
Li ₂ O/HT-9	550	7.5 x 10 ² He (Static)	410	4.0	30	Li ₅ FeO ₄ , LiCrO ₂	Li ₅ FeO ₄	5
	650	" "	1035	42	40			5
Li ₂ O/Incoloy 800	650	7.5 x 10 ² He (Static)	410	1.61	10.25			3
	700	" "	410	1.70				3
	750	" "	410	1.92	10.34			3
					42.1 ± 3.0 (gb)			
Li ₂ O/Incoloy 800					46.1 ± 3.2 (gb)			
	800	10 ⁻⁵ (Dynamic)	100	0.19 ± .1	5.0 ± 1.6	LiCrO ₂	Li ₅ FeO ₄	2
					5.4 ± 5.1	"	"	"
	850	" "	"	+ 0.70	15.8 ± 4.3	"	"	"
					17.4 ± 5.4	"	"	"
	875	" "	"	+ 1.15	28.4 ± 3.9	"	"	"
					36.6 ± 7.4	"	"	"
	900	" "	"	+ 2.67	48.7 ± 10.8	"	"	"
					59.9 ± 7.2	"	"	"
	950	" "	"	+ 5.92	101.0 ± 13.7	"	"	"
					130.1 ± 1.6	"	"	"
	1000	" "	"	+11.78	195 ± 21	"	"	"
					238 ± 14	"	"	"
	1050	" "	"	16.61	325 ± 16	LiCrO ₂	Li ₅ FeO ₄	2
					332 ± 31	"	"	"
	1100	" "	"	22.15	367 ± 15	"	"	"
					390 ± 27	"	"	"

FIGURE 5.2.1 LITHIA/METAL COMPATIBILITY RESULTS
(CONTINUED)

REACTION COUPLE	TEMP. °C	TEST CONDITIONS ATMOSPHERE (TORR)	TIME (HRS)	WT. CHANGE (MG/CM ²)	EFFECT ON METAL SCALE TH. (μm)	IMPURITY	EFFECT ON CERAMIC REF.
Li ₂ O/ Hastelloy X-RB	500	7.5 x 10 ² He (Static)	410	0.57	3.21		3
	550	" " "	"	0.81	5.48		
	600	" " "	"	0.68	3.28		
	650	" " "	"	0.87	6.16		
	700	" " "	"	1.00	-		
	750	" " "	"	0.97	5.74		
	800	10 ⁻⁵ (Dynamic)	100	+ 0.10	1.5 + 0.4	LiCrO ₂	Li ₅ FeO ₄ 2
					1.7 + 0.4	" 2	"
	850	" "	"	+ 0.10	2.1 + 0.3	"	"
					2.4 + 0.6	"	"
	875	" "	"	+ 0.29	3.1 + 1.0	"	"
					2.6 + 0.7	"	"
	900	" "	"	+ 0	3.2 + 1.0	"	"
					2.9 + 0.9	"	"
	950	" "	"	+ 0.1	7.4 + 2.5	"	"
					8.3 + 2.0	"	"

conducted from 500⁰-1100⁰C, in vacuum or He atmospheres, and for various lengths of times, 100-1035 hours. The results are listed in Figure 5.2.1 and of these only pure Ni appears to be relatively inert when in contact with Li₂O. The metal compositions have been outlined in Figure 5.2.4. The 316 SS starts to react severely after 950⁰C, although there is grain boundary attack at 600⁰C. The metal samples tested at temperatures of 950⁰-1100⁰C revealed significant weight gain (Δw) and oxide scale formation (identified as LiCrO₂), while Li₅FeO₄ appeared on the Li₂O surface. A 20 mil vapor-deposited Ni coating on the 316 SS lowered both the metal's weight gain and oxide scale formation (LiCrO₂) and prevented the appearance of any Li₅FeO₄ on the Li₂O surface. The Ni coating together with the LiCrO₂ formation was thought to play a role in inhibiting the Fe diffusion to the Li₂O surface.

The Li₂O/Incoloy 800 couple showed significant scale formation (15 μ m) @ 850⁰C and again revealed LiCrO₂ on the metal and Li₅FeO₄ on the surface of Li₂O. At 100⁰C, the weight gain of the metal is twice that of 316 SS but the oxide scale was only 50% greater. At the lower temperatures, especially in stagnant He, there is not too much change in weight between the Incoloy 800 and the 316 SS but the oxide scale was only 50% greater. At the lower temperatures, especially in stagnant He, there is not too much change in weight between the Incoloy 800 and the 316 SS but there is twice as much grain boundary attack in the Incoloy 800.

The Li₂O with Hastelloy X-R lasted until 1000⁰C under vacuum before succumbing to marked attack. However, even at the higher temperatures it is 1/3-1/2 the amount of reaction of the 316 SS; this difference is probably due to its higher Ni content and lower Fe contents.

The Li₂O/Inconel 600 couple did not show the expected improvement with increasing Ni content. Its results were slightly higher than those of the Hastelloy X-R despite the increase in Ni and decrease in Fe contents with that of Inconel. Again LiCrO₂ and Li₅FeO₄ were seen as the major contaminants at the high temperatures (+ 800⁰C).

The $\text{Li}_2\text{O}/\text{HT-9}$ couple showed 4-5 times the reaction of the 316 SS at higher temperatures in a static He environment. In addition, Li_3FeO_2 was also seen in the scale on the metal and not just on the ceramic surface as before.

Since oxide scale formation can be described by a parabolic function $w^2 = kt$ (where w^2 = the weight change or oxide scale thickness, t = reaction time, and k = the rate constant), a plot of k versus $1/T$ was made (Figure 5.2.2). Since Ni interaction with Li_2O was so minute, no data were available for the graph. The Mo alloys show the least oxide scale formation when compared to the Fe-Ni-Cr alloys, especially at low temperatures. Hastelloy X-R is the best in comparison with 316 SS, Incoloy 800, and Inconel 600 although, at temperatures $\approx 800^\circ\text{C}$, it approaches the same reactivity as 316 SS. The Incoloy 800 follows fairly closely the reactivity of 316 SS, while Inconel 600 behaves like Incoloy 800 at temperatures below $\approx 850^\circ\text{C}$ and behaves like 316 SS at higher temperatures. The results for the Hastelloy X-R are attributed to the Mo addition which counters its higher Fe content compared to Inconel 600. The data were generated (four couples) in a dynamic 10^{-5} vacuum, yet Li_2O vaporization has not been addressed, especially at the higher temperatures ($> 1000^\circ\text{C}$).

Figure 5.2.3 is a similar plot for temperatures below 700°C and static He. The slope has radically changed for Hastelloy X-R, almost exhibiting no temperature dependence. At the lower temperatures, the Inconel 600 performed better than the 316 SS, as would be expected with its low Fe and high Ni concentrations. The Incoloy 800 has maintained its previously seen relationship to 316 SS despite its compositional differences. Hastelloy X-R is still the best of the Fe-Ni-Cr alloys because of its nonresponse to temperature, although the 316 SS provides better resistance to the Li_2O at temperatures below 600°C . Comparison of the data presented in both figures is difficult since atmosphere seems to play a big role in the diffusion kinetics. It is hard to imagine that the reactivity of the metal is any different under vacuum than He, but the ceramic may be another matter. The presence of LiOH or Li_2CO_3 has been hypothesized as the reactive species instead of Li_2O itself. In all the studies, the presence or lack of presence of these two compounds is not actively discussed.

FIGURE 5.2.2 RATE OF OXIDE SCALE FORMATION ON METAL/Li₂O REACTION COUPLES IN A 10⁻⁵ TORR ENVIRONMENT

FIGURE 5.2.3 RATE OF OXIDE SCALE FORMATION ON METAL/Li₂O REACTION COUPLES IN A STATIC He ENVIRONMENT

FIGURE 5.2.4 CHEMICAL COMPOSITIONS OF METAL REACTION COUPLE SPECIMENS (WT%)

	316 SS	INCOLOY 800	HASTELLOY X-R	INCONEL 600	Ni	Mo (sin)	Mo (EBM)	TZM
Fe	69.79	43.8	18.4	8.13	0.03	-	.0002	.002
Ni	10.14	33.2	49.5	74.96	99.56	-	.0001	.001
Cr	16.83	20.7	22.0	16.16	-	-	-	-
Mo	2.10	-	8.81	-	-	99.8	99.95	99.83
Al	-	0.04	0.02	-	-	-	-	-
Ti	-	0.36	0.02	-	-	-	-	.04
Mn	0.72	0.9	0.65	0.21	0.26	-	-	-
Si	0.36	0.31	0.03	0.39	0.03	-	.0066	.001
P	0.035	-	-	0.008	-	-	-	-
S	0.02	0.0005	-	0.002	-	-	-	-
C	0.07	0.03	0.08	0.04	0.09	.002	.008	.024
Cu	-	0.21	-	0.02	0.03	-	-	-
O	-	-	-	-	-	-	.0005	.0006
Zr	-	-	-	-	-	-	-	.092

5.3 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM

Hollenberg⁽⁴⁾ studied $\gamma\text{-LiAlO}_2$ interactions with 316 SS or Ni 270 @ 600°C for 98 days. In addition, he investigated $\gamma\text{-LiAlO}_2/\text{Ni 270}$ @ 750°C for 98 days. In all three cases negligible interaction was detected. His samples were encapsulated in a stainless steel cup sealed in a dry inert gas atmosphere. Each sample was then heated individually by resistance heated furnaces, which maintained a constant temperature $\pm 10^\circ\text{C}$.

5.4 $\text{Li}_2\text{O}-\text{SiO}_2$ SYSTEM

Hollenberg⁽⁴⁾ used Li_4SiO_4 85% TD and Ni 270 or 316 SS @ 600°C for 98 days and Ni 270 at 750°C for 98 days. In all three cases the Li_4SiO_4 pellets were sandwiched between either Ni 270 or 316 SS in a stainless steel cup and encapsulated in a dry inert gas atmosphere. The results of his study indicate that negligible interaction occurred between the Li_4SiO_4 and the two metals.

5.5 $\text{Li}_2\text{O}-\text{TiO}_2$ SYSTEM

Finn et al.⁽⁵⁾ formed a Li_2TiO_3 /alloy coupled with HT-9, 316 SS, and Ni coated (20 μm) 316 SS and heated them to 650°C for 410 hours or @ 550°C for 1035 hours in 10^5 Pa static helium atmosphere. They found that a slight amount of scale formed on all three metals, with the Ni coated 316 SS showing the most and HT-9 the least amount. In all three, LiCrO_2 was the major and LiFeO_2 the minor contaminant. They believed that the formation of significant amounts of LiCrO_2 acted as a barrier to LiFeO_2 formation. In any event, the amount of scale was $\approx 1/2$ that of the Li_2ZrO_3 couples, and $1/6$ of the amount of penetration incurred using Li_2O couples of the same three metals. Although no scale was formed on the Li_2TiO_3 samples, the TiO_2 content on the surface increased, verifying the transport of lithium to form the scale on the metal.

5.6 $\text{Li}_2\text{O}-\text{ZrO}_2$ SYSTEM

Finn and co-workers⁽⁵⁾ studied the reaction of Li_2ZrO_3 (88% TD) with HT-9, 316 SS and Ni coated 316 SS (20 μm) substrates. The sandwich arrangements

were held @ 650°C for 410 hours or @ 550°C for 1035 hours in $\sim 10^5$ Pa static helium environment. Their results indicate severe interaction with the HT-9 metal, with the Ni coated 316 SS showing the least. The scale formed on the HT-9 was identified as LiFeO_2 with a small amount of LiCrO_2 . The 316 SS again revealed LiFeO_2 with a minor amount of LiCrO_2 . The Ni coated 316 SS showed the least amount of contamination, with LiCrO_2 being the major contaminant identified and a minor amount of LiFeO_2 . Although no scale was formed on the Li_2ZrO_3 , the amount of ZrO_2 was increased at the surface, corresponding to the loss of Li_2O to form the scale on the metal.

Hollenberg⁽⁴⁾ encapsulated a Li_2ZrO_3 sample 75% TD with Ni in a stainless steel cup sealed in a dry inert gas and heated in a resistance furnace for 98 days @ 750°C. He found no formation of any new phases on either surface and essentially no interaction.

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