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PROSPECTIVE MATERIALS FOR A TARGET ELEMENT FOR THE CO-PRODUCER PROGRAM

By

J. W. Carter

May 15, 1964

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I. INTRODUCTION

Prospective materials for a lithium bearing target material for use in the N Reactor must fulfill a double set of requirements. The first set of requirements pertain to the properties necessary for use under normal operating conditions. The second, and more severe set, place limits on the behavior of the target material during the maximum credible incident. The maximum credible incident consists of a loss of primary coolant, followed by failure of the backup water supply system. A temperature transient reaching a maximum of from 800 to 1200°C is anticipated for a period of approximately two hours. These two sets of requirements must be met in order to insure safe operation of the reactor.

It is planned to can the lithium bearing material in a double container. The inner container of aluminum will be enclosed in a Zr-2 can, with an unbonded surface between the two. The aluminum can is desirable for handling and shipping reasons. Also, it is an effective barrier to the tritium produced in the $Li^6 + n \longrightarrow T + \alpha$ reaction. The unbonded surface provides an additional barrier to tritium movement.

The normal environment for the element is water at a temperature of up to 300°C and a pressure of 1400 psi. Inlet pressure is 1450 psi while outlet is 1350 psi. The co-producer element consists of a tubular driver component with the target rod centered within the driver. Coolant will flow down the annulus between the target and driver components.

The necessary material properties for use under normal operating conditions will be discussed, followed by a discussion of those necessary to insure safety during a maximum credible incident. A number of potential lithium bearing materials will be examined in light of these requirements.

Since Li-Al and Li-Mg alloys have been discussed extensively elsewhere, they will not be covered in this paper. This leaves the ionic, covalent, and glass forming compounds of lithium as potential candidates. Lithium bearing cermets are also of great interest and will be included.

II. MATERIAL REQUIREMENTS

A. Normal Operating Conditions

1. Lithium Density

The first requirement for a target material is that it possess an adequate lithium density. If a lithium compound enriched in Li^6 is used, the problem is a minor one, since a marginally usable compound could be enriched to attain an economical Li^6 density. For natural lithium bearing materials, which contain 7.42% Li^6 and 92.58% Li^7, there is a lower limit on the lithium density. All materials with a lithium density of approximately 0.10 g/cc or greater will be considered in this study. However, recent information indicates that the equivalent of a 3 w/o Li-Al alloy, 41% enriched in Li^6, will be necessary. This means that a material must have an Li^6 density of 0.0308 g/cc and a natural lithium density of 0.~~415~~ g/cc.

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2. Compatibility With Aluminum

The second criterion requires that the lithium compound not react with its aluminum can. This includes all chemical reactions that might damage either the target material or the can. Since it is desirable to use an aluminum can, the inertness of the target material relative to aluminum is a prime consideration.

3. Behavior in Hot H_2O

A defect in the Zr-2 cladding will lead to corrosion of the aluminum can. If this is not detected in time to prevent failure, the target material will be exposed to the primary coolant. The behavior of the material under these conditions is of interest, since excessive corrosion and release of radioactivity to the coolant must be avoided. There are two possible mechanisms by which the target material can release radioactive elements, chiefly tritium, to the primary loop coolant. The first mechanism is by reaction with the water. Some lithium compounds react violently with water, generating a gas and a water soluble compound in solution. This type of behavior is unacceptable. More often, the target material will simply dissolve or decompose. It may be possible to use such materials, if it can be determined that the rate of dissolution is slow enough.

4. Tritium Loss Rate

Another requirement, important from both the safety and economic viewpoint, specifies that the tritium loss rate from the normal, undefected, element must be low. The design of the entire element has a great effect on the T loss rate. The rate is lower for an unbonded surface than for a bonded one. Thus, the target material should not be bonded to the Al can, nor should the Al can be bonded to the Zr-2 cladding. The target material should retain the tritium in the lattice, if possible, and should also retain the He. If the He is allowed to coalesce, it tends to fracture the target material, allowing the tritium to escape. This is the mechanism for tritium release in Li-Al alloys. It should be less of a problem in other materials, but it is necessary that the helium be retained in order to keep the internal pressure down.

5. Lithium Loss Rate

Another important property a potential target material must possess is a negligible lithium loss rate at 300° C. The lithium atom is small enough to diffuse through to the coolant if an appreciable concentration in the vapor phase were maintained in the interior.

B. Maximum Credible Incident

1. General Requirements

With N Reactor loaded for co-product operation, a substantial amount of the reactor control is contained in the target rods. If the

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target material were to be completely removed from the reactor, control of the reactor would be lost(14). The extent to which relocation or partial loss of the lithium can safely occur is not known. Therefore, a firm, quantitative statement of the required material properties cannot now be made. Lacking something better, the analysis made for the temperature transient for a standard fuel loading during Phase I operation can be used as a first approximation. The analysis indicates that uranium temperatures up to 1100-1200 C will be reached(15) and that the central one-sixth of the fuel load will be molten for up to 2.7 hours after the incident(16). Assuming that the tube-and-rod element to be used for co-producer operation will suffer the same temperature transient during the design maximum credible incident, the target rod, located within the fuel component, will be subjected to nearly the same temperature conditions as the fuel. Although further analysis may show that some lithium loss (e.g. by vaporization) or relocation (e.g. by flow of molten target material or by distillation) may be permissible, the target element, ideally, should suffer <u>no</u> loss or relocation of lithium and the materials should undergo <u>no</u> chemical reaction with other materials present which releases a large amount of energy over a short period of time. Lacking detailed quantitative requirements for the target element and the materials used therein, the discussion to follow is, of necessity, qualitative and comparative.

The three main requirements--high temperature stability, ease of extraction, and low cost--appear now to be incompatible. The final choice of the target material, as seen now, will be one which has enough thermal stability to withstand the transient but not so much that extraction is too difficult.

2. Compatibility with Aluminum

The aluminum can containing the target material will melt around 660° C. In order that target element integrity be maintained up to high temperatures, the lithium compound must not undergo any rapid reactions with the molten aluminum. Reactions that liberate either heat, or gas, or lithium in an elemental form are to be avoided.

3. Helium and Tritium Loss Rates

The He and T loss rates for the target material should be low. High loss rates cause high internal pressure in the target element and may lead to early failure. If these gases are retained in the lattice of the target material the containment time will be increased.

4. Lithium Loss Rates

One of the most important properties that a target material can possess is the ability to retain lithium in the temperature range from 800° C to 1200° C. Vaporization is one of the two main mechanisms by which lithium can leave the reactor. The other mechanism is the transport of the target material by the molten aluminum, if any aluminum remains unalloyed with the Zr-2. It is expected that vaporization will be the primary mechanism.

5. Summary

The properties required of a target material for use during the design maximum credible incident are interrelated. The goal to be attained is the safe and positive control of the reactor during and after the incident. There should be no reaction with molten aluminum that would generate large amounts of heat, free lithium, or gas pressure. The He and T release rate should be low in order to avoid high internal pressures in the element. The lithium loss rate should be low.

III. MATERIALS EVALUATION

A. General Comments

In this section, various lithium compounds will be examined for use as target materials, in light of the stated requirements. The ionic, covalent, and glass forming compounds of lithium, as well as some lithium bearing cermets, will be discussed. Twenty-eight compounds have been chosen for analysis. Compounds are included if they possess a lithium density of 0.1 g/cc or greater, and a melting point of over 250° C. Organic compounds have been excluded because of their instability under irradiation. Intermetallics have also been excluded due to the lack of information on them. The only two that could be found that meet the initial criteria are Li_3Sb, with a melting temperature of over 950° C, and Li_3Bi, which has a melting temperature of 1145° C. Nothing further could be found concerning these intermetallics. A summary of some of the properties of interest for the compounds chosen has been made in Tables I, II, III, and IV.

B. Discussion

1. Halides

The first compounds to be considered are the halides: LiCl, LiBr, LiI, and LiF. All four of these compounds have a respectable lithium density, with the LiF having the highest at .696 g/cc. The chloride, bromide, and iodide are all very soluble in water, and have low melting points compared to the fluoride.(1) The fluoride is insoluble in water and has a melting point of 840° C. The boiling point is 1681° C. Lithium fluoride has been used to produce tritium in the Hanford reactors, but was prone to swelling and rupture of the slugs. It was reported to have been caused by the release of free F_2, but this interpretation has been questioned recently.(2) The lithium halides all have the cubic (NaCl) structure. The vapor pressures for all except the fluoride are well over 100 mm of Hg at 1200° C, thus placing a great deal of lithium in the vapor phase. For this reason, as well as the low melting points and high solubility, LiCl, LiBr, and LiI, must be rejected. LiF must also be rejected because no fluorine, either in element or compound form, can be tolerated in the system due to the danger of rapid chemical reactions or corrosion. The other halides would also be likely to increase the corrosion rate.

2. $LiNO_3$

Lithium nitrate has a sufficient lithium density to be considered for service. However, it is very soluble in water and would be molten at normal operating temperature, since it melts at 254° C.(3) Upon heating to 600° C, it decomposes with the liberation of oxygen and nitric oxides.(3) Its effects on aluminum are not known. A further deficiency is that the material is incapable of holding the He and T at operating temperature. This compound does not possess the stability required of a satisfactory target material.

3. Li_2CO_3

At first glance, lithium carbonate, Li_2CO_3, would appear to be a possible candidate. It has a fairly high melting point (735° C) and is only moderately soluble. However, it dissociates into Li_2O and CO_2 upon heating past the melting point.(3) The reaction medium is quite corrosive, attacking platinum. There is also a reaction that occurs between the carbonate and aluminum. The reaction is:

$$3Li_2CO_3 + 2Al \longrightarrow Al_2O_3 + 6Li + 3CO_2$$

It is a violent reaction, liberating heat, gas, and elemental lithium. This compound might be acceptable at normal operating temperatures, although oxidation of the aluminum would probably take place. Its behavior at high temperatures leaves much to be desired.

4. Li_2SO_4

Lithium sulfate, Li_2SO_4, has a melting point of 859° C and is very soluble in water.(3) The lithium density is .280 g/cc. The room temperature form is the hexagonal or orthorhombic β, which transforms to the cubic α at 500° C.(3) Aside from its high solubility in water, the material appears to be relatively innocuous. The vapor pressure might be as low as that of lithium fluoride. Unfortunately, no data is available to confirm this supposition. This compound might be worthwhile looking at more closely, if it is felt that a molten salt, with consequent gas release, would be acceptable at maximum transient temperature.

5. Li_3N

Lithium nitride is not worthy of detailed consideration, but is included for completeness. It has a melting point of 856° C. The most detrimental property it possesses is a tendency to react violently with water according to the equation:

$$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$$

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At 800°C it attacks iron, nickel, copper, platinum, quartz, and porcelain.(3) Its use in a reactor would be most hazardous.

6. Li_2C_2

Lithium carbide, Li_2C_2, is a brittle substance with a lithium density of .610 g/cc. It dissociates to metallic lithium and graphite on heating. A reaction takes place with water to produce acetylene and lithium hydroxide.

$$Li_2C_2 + 2H_2O \longrightarrow 2LiOH + C_2H_2$$

It does not appear that lithium carbide has much future as a target material.

7. $Li\ SO_3F$

Lithium fluosulfonate shows very little potential as a target material. The melting point is only 360°C. It is very soluble in water and has the added disadvantage of containing fluorine.

8. $Li\ GaN_2$

Lithium gallium nitride also has several bad characteristics. The cross-section of gallium is 30 barns. This is entirely too high. It also decomposes in hot water. The decomposition point is 800°C, well below the maximum possible temperature.

9. LiH

Lithium hydride has a high lithium density, about .686 g/cc. The melting point of 688°C is too low, and the compound decomposes completely at 850°C. LiH reacts with water to give LiOH and H_2.

$$LiH + H_2O \longrightarrow LiOH + H_2(g)$$

10. $Li\ MoO_4$ and $Li_2\ WO_4$

Lithium molybdate and lithium tungstate are unsuitable because of their low melting temperatures and their high solubilities. The nuclear cross-sections for these compounds are rather high since molybdenum and tungsten have high cross-sections, 2.7 barns and 19 barns, respectively.

11. $Li_2\ GeO_3$

Lithium metagermanate has a high melting point and is not very soluble in water. However, the cross-section of germanium is 2.4 barns, an order of magnitude greater than those of aluminum or silicon. Germanium is also a more costly material than the other potential compounds. No information is available on the vapor pressure or other properties of this compound.

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12. $LiOH$

Lithium hydroxide is the least soluble of the alkali metal hydroxides. However, it is still soluble to the extent of 5.4 moles/l. at 30° C. The melting temperature is 450° C, and complete decomposition to lithium oxide and water takes place near 1000° C. It is also quite corrosive at high temperatures. LiOH does not appear to have much potential as a target material.

13. Li_3PO_4

Lithium orthophosphate has a melting temperature of 837° C, somewhat below the maximum possible transient temperature. It is only slightly soluble in pure water, but the solubility increases greatly in ammonia water. The lithium density meets the latest requirements, but the fact that this compound is molten at the maximum transient temperature precludes it from any further consideration.

14. $Li_3Na_3\ (AlF_6)_2$

Lithium sodium fluoaluminate has a melting temperature of 710° C and is only slightly soluble in water. However, the fact that it contains fluorine, in addition to the low melting point, makes this compound unusable as a target material.

15. Li_2O

The next compound of interest is lithium oxide, Li_2O. This oxide is thermally stable and very refractory. The lithium density is the highest of any listed at .931 g/cc. Values for the melting and boiling temperatures are subject to some disagreement. The melting point is somwhere between 1427° C(1) and 1570° C(3). The boiling point has been reported as 1527° C(1) and 2600° C(3). The melting point in either case is well above the transient temperature. Sublimation of the compound begins in the 800° C - 1000° C range. The vapor pressure is greatly increased by the presence of water vapor. Table V shows this behavior.(3) The reaction is assumed to be:

$$Li_2O + H_2O \longrightarrow 2LiOH(g)$$

Lithium oxide is very soluble in water and is also hygroscopic. In the over 1000° C temperature range it is extremely corrosive, attacking most metals and oxides. Also, aluminum will reduce lithium oxide to metallic lithium in this temperature range. Lithium oxide would appear to be a very dubious prospect at 300° C due to its high solubility. At maximum transient temperature, a combination of high lithium loss rate in a water vapor containing atmosphere, and the corrosiveness of the material make it unsuitable for use.

16. $LiAlO_2$ and $LiAl_5O_8$

Lithium aluminate, $LiAlO_2$, is a high melting point ceramic. The

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melting temperature is 1610° C.(4) Lithium density is about .268 g/cc, and the compound is insoluble in water. The vapor pressure of Li_2O over the compound is negligible up to 1200° C. At 1400° C, it increases, and by 1700° C it is appreciable. In the range of interest, then, lithium aluminate has an acceptably low vapor pressure. It is possible that some reaction with aluminum may take place at elevated temperatures. However, it is doubtful that the reaction would be rapid enough to reduce any lithium before the aluminum had alloyed with the Zr-2 cladding. Lithium aluminate is a good prospect for a target material and thus deserves added analysis.

The structure of lithium aluminate may be either rhombohedral (α) or tetragonal (γ).(5) The rhombohedral form is the low temperature structure which changes to the tetragonal high temperature form at 900° C. The transformation of $\alpha \rightarrow \gamma$ is essentially irreversible, although α can be produced by prolonged grinding of the γ. The molecular volumes and densities of the two forms are: $Vm(\alpha) = 32.205 \text{ Å}^3$, $\rho_\alpha = 3.4$ g/cc, $Vm(\gamma) = 42.775 \text{ Å}^3$, $\rho_\gamma = 2.56$ g/cc. The density normally given in data compilations for this compound is 2.55 g/cc; it is difficult to produce without heating the reactants, Li_2O and Al_2O_3, to well over 900° C. Material in the high temperature form avoids the 30% volume increase at the transformation temperature. This volume change would be quite inconvenient in a target element, so it is fortunate that the transformation is essentially irreversible. However, tests should be carried out to determine if the transformation will occur after long periods at 300° C. If it does, a slow shrinkage will take place that might cause buckling of the element.

The coefficient of expansion of $LiAlO_2$ is $12.4 \times 10^{-6} \cdot C^{-1}$, about half that of aluminum and twice that of Zr-2.(6) Appendix I contains an analysis of target element behavior during startup. No problems are expected if an expansion gap is built into the design to allow for the difference in longitudinal expansion between the aluminate and the Zr-2 can.

The thermal stresses created by either a scram or the rapid heatup associated with a maximum credible incident could possibly cause fracture of the lithium aluminate. Appendix II shows a calculation of the maximum allowable heating or cooling rate, assuming a 100% dense material and reasonable values for the material properties. The allowable rate of temperature change is less than that possible in either a scram or a maximum credible incident transient. However, fracture of the material may not be harmful if the gas retention properties are not significantly altered or the fragments of material excessively small.

It is expected that lithium aluminate will possess gas retention properties on a par with similar ceramic materials. Lithium aluminate is a compound formed from Li_2O and Al_2O_3 and is similar in its general nature to these two materials. It is reasonable to expect that many of its properties will be intermediate to those of Li_2O and Al_2O_3. The extent to which $LiAlO_2$ is water soluble would tend to indicate that it may be closer to the Al_2O_3 in behavior.

Since Al_2O_3 retains Xe^{133} about as well as UC or UO_2 it is very likely that $LiAlO_2$ will retain its gas burden equally well. (17) UC and UO_2 are both considered to exhibit excellent fission gas retention properties. Therefore, the aluminate should retain most of the helium and tritium in the lattice at normal operating temperatures. At high temperatures, release should be delayed to a great extent. It is apparent that $LiAlO_2$ has a great deal of potential as a target material.

The next compound to be considered lies in the same binary phase diagram as $LiAlO_2$. This diagram is shown in Figure I. (5) $LiAl_5O_8$ is a more refractory compound than $LiAlO_2$, with a melting point of 1950° C. (5) The boiling point is unknown. The phase diagram indicates that an order-disorder reaction takes place in the $LiAl_5O_8$ at 1300° C. (5) This is open to question since the experimental data available can be used to support a reconstructive type transformation as well. (7) This transformation is of no practical importance since it takes place at a higher temperature than the expected transient, and causes less than a 1% volume increase. The structure of $LiAl_5O_8$ is cubic at low temperatures, and a spinel form above the transformation temperature. (5,7) Because of its kinship to $LiAlO_2$ and Al_2O_3, the gas retention properties of $LiAl_5O_8$ should be quite good. It is also likely to be insoluble since both $LiAlO_2$ and Al_2O_5 are. Lithium loss rate is lower than that of $LiAlO_2$, and is negligible below the 1400° C - 1700° C temperature range.

The response of $LiAl_5O_8$ to thermal variations is more favorable than that of $LiAlO_2$. The coefficient of thermal expansion for $LiAl_5O_8$ is 8.2×10^{-6}°C^{-1}. (6) Fracture resistance should be higher and expansion lower than in the case of the aluminate. In fact the only property in which the spinel is inferior to $LiAlO_2$ is in lithium density. The lithium density of the $LiAl_5O_8$ is only 0.094 g/cc. It is doubtful that this will be adequate. However, there is a possibility that a composition falling in the region on the phase diagram between $LiAlO_2$ and $LiAl_5O_8$ will be most suitable for the task. The phase diagram shows only a mixture present, but more recent work indicates that a solid solution exists in this region. (8) Thus, it may be possible to blend Li_2O and Al_2O_3 in the proportions necessary to achieve an optimum lithium density.

17. Lithium Silicates

Another compound of interest is lithium silicate, Li_2SiO_3. The lithium density is about .356 g/cc. There are several marginal properties of this compound that may discourage its use. The melting point is 1201° C, just beyond the maximum expected transient. It is remarkably corrosive, though this may not be too important due to the short containment time necessary. The vapor pressure is unknown, but is probably greater than that of the aluminate, since the melting temperature is lower. This indicates that the thermal stability is less, which usually leads to a higher vapor pressure.

Two other lithium silicates also exist. (9) The phase diagram in Figure II shows the relationship between these materials and

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LiSiO$_3$. The high silica compound, $Li_2O \cdot 2SiO_2$; has a lithium density of .233 g/cc and a melting point of 1033° C. The low silica compound, $2Li_2O \cdot SiO_2$, has a lithium density of .540 g/cc and a melting point of 1250° C. Both of these materials probably decompose in hot water, because the intermediate composition, $Li_2O \cdot SiO_2$, and also the Li_2O, decompose in this medium. It is likely that the low silica one is more susceptible to this, since it contains the most Li_2O, which is the soluble component in the material. The silicates show fair potential for use as target materials. However, their greater corrosiveness, vapor pressures, and water solubilities make them less promising than the aluminates. Also, the high silica $Li_2O \cdot 2SiO_2$ cannct be used if the maximum transient temperature is more than 1000° C.

18. Lithium Aluminosilicates

The aluminum aluminosilicates are another group of materials which show signs of promise. The phase diagram for the $Li_2O \cdot Al_2O_3 - SiO_2$ system is shown in Figure III.(9) The two compositions of interest are $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ and $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$. These compounds have melting temperatures of 1390° C and 1420° C respectively. They are probably less soluble in water than are the silicates; it is doubtful that they are as good as the aluminates in this respect. This type of behavior is expected since the aluminosilicates can be looked at as being $LiAlO_2$ with SiO_2 added. The addition of the SiO_2 lowers the melting temperature, and it is reasonable to assume that the solubility in water will be increased as the material moves closer to the lithium silicates in composition. The same relationship would be likely to occur where the vapor pressure and the corrosive properties are concerned; i.e., the aluminosilicates will be intermediate to the silicates and aluminates. Gas retention properties should be excellent - about the same as for the aluminates and silicates, since these materials are similar in nature to the aluminosilicates.

One advantage that the aluminosilicates possess is a low or negative coefficient of thermal expansion.(6) $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ has a coefficient of $.9 \times 10^{-6}\ °C^{-1}$. This is a factor of 27 less than the coefficient of expansion for aluminum and one seventh of that for Zr-2. Thus, there is no necessity for an expansion gap in the element. $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ is unusual in this respect; the coefficient of thermal expansion is a $-6.5 \times 10^{-6}\ °C^{-1}$. The material contracts when heated. The 1:1:3 composition, which lies in the solid solution region between the above two compounds, has a coefficient of expansion of $-.9 \times 10^{-6}\ °C^{-1}$. It should be possible to adjust the coefficient of expansion by varying the amounts of 1:1:2 and 1:1:4 compounds that go into the material.

19. Li_2TiO_3 and $LiBO_2$

To complete this general discussion of potential target materials, two more compounds must be considered. Lithium metatitanate, Li_2TiO_3, is composed of equimolar portions of lithium oxide and

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titanium oxides up to at least 1054°C$^{(10)}$, and has a melting point of from 1520 - 1564°C.$^{(11)}$ The lithium density is approximately .33 g/cc. The vapor pressure of Li_2O over the compound at 1200°C is probably about the same as for the aluminosilicates, since the melting temperatures are about the same. Titanium oxide is insoluble in water, but is soluble in alkaline solutions. Lithium metatitanate may be more soluble than this. The only real disadvantages in using Li_2TiO_3, as far as can be determined from the data available, are material cost and the high cross-section of titanium. The cross-section of titanium is 5.8 barns, significantly higher than the cross-sections for aluminum or silicon.

The final material to be considered is $LiBO_2$. This compound has a melting temperature of 846°C and a lithium density of .307 g/cc. It may decompose in hot water. No matter what the physical properties are, the high cross-section of boron (755 barns) is enough to disqualify this material.

20. Cermets

Lithium bearing cermets, containing one of the compounds discussed above in a Zr-2 or aluminum matrix, are also potentially useful target materials. A cermet would be advantageous from the point of view of retaining released fission gases and protecting the ceramic from the primary coolant should a defect occur. The two potential matrix metals, Al and Zr-2, each have low cross-sections (.23 and .18 barns, respectively). Aluminum has further advantages in that it is easy to work and relatively inexpensive. The disadvantages in using aluminum are its low melting point and poor resistance to corrosion by the alkaline coolant. The major disadvantages in using Zr-2 are its cost and the lesser workability, compared to aluminum. Its advantages lie in its high melting point and similarity of thermal expansion coefficient to those of some of the more promising ceramic materials. The expansion coefficient of aluminum is so much greater than that of any of the potential target materials that it would be hard to achieve a void free cermet during temperature transients. This would be less of a problem with Zr-2. There should be no problem in making cermets of this type. Whether they are worth the extra cost and increase in cross-section is another matter.

III. FABRICATION

A. General Comments

The ease with which a target material may be fabricated plays an important part in the over-all economics of tritium production. The relative fabricability of the three promising classes of target materials will now be examined. In addition, the problems of cermet fabrication will be considered. The three classes of lithium bearing compounds that meet the in-reactor criteria are: the lithium aluminates ($LiAl_5O_8$, $LiAlO_2$), the lithium silicates (Li_2SiO_3etc), and the lithium aluminosilicates ($Li_2O.Al_2O_3.2SiO_2$, $Li_2O.Al_2O_3.4SiO_2$). From the standpoint of fabricability, it is necessary only to cover each class rather than each compound.

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B. Discussion

1. Lithium Aluminates

The aluminates are hard, covalent crystals; they are also non-glass-formers. Since they have high melting temperatures and a tendency to lose lithia below the melting temperature, it is unlikely that fusion casting will be an economical or convenient method of making target shapes from these materials. A more likely method would be some type of pressing or forming operation followed by sintering. Probably some other compound will have to be added to improve the sintering characteristics, as they do not appear to be outstanding. Another promising type of operation is swaging an aluminum tube of aluminate particles down to the proper size. The major difficulty with sintering or swaging as a means of fabrication is that high density material is much harder to obtain than in fusion casting. Fusion casting is generally less expensive than these two methods, also.

2. Lithium Silicates

The lithium silicates appear to be far easier to fabricate than the lithium aluminates. This material could be fabricated by any of the three means mentioned above. It is possible to make fusion cast glasses from the $Li_2O \cdot 2SiO_2$ and the $Li_2O \cdot SiO_2$ compositions.(12) This should be cheaper than either swaging or sintering. A higher density may also be obtained, if such is found to be desirable. The advantage of the glassy structure lies in its superior ability to retain fission products. The open structure of the glass leaves many unfilled spaces among the constituent atoms of the lattice. Helium and tritium atoms may fill these holes, so that fragmentation of the material by coalesced gas does not occur. Thus, two of the lithium silicates appear to have superior properties insofar as fabrication is concerned.

3. Lithium Aluminosilicates

The ease of fabrication of the lithium aluminosilicates is probably intermediate to that of the aluminates and silicates. It should be possible to fusion cast either glasses or crystalline materials, although the compounds to be considered are somewhat less prone to glass forming than the silicates. Swaging or sintering are also possible; they are likely to lead to a lower density material. The higher melting temperatures will increase the problems of forming these materials by any of the above methods; the fusion casting process will suffer the most.

From the foregoing discussion, it can be seen that the ease of fabrication of the prospective target materials varies to a significant degree. The lithium silicates are the most easily formed, followed by the aluminosilicates and the aluminates.

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4. Cermets

There are several ways to fabricate lithium-bearing cermets having an aluminum or Zr-2 matrix. Nuclear Metals has produced sintered aluminum powder (SAP) - Li_2SiO_3 and SAP - $LiAlO_2$ cermets by cold pressing and extrusion.(11) The strength characteristics at elevated temperatures were found to be superior to aluminum-lithium alloys, but helium gas retention in a SAP cermet was greatly inferior. In this case, the gas was produced in the cermet by bombardment with alpha particles. In a lithium-bearing cermet the gas is expected to remain in the lithium compound, so this behavior is not as important as might be thought at first. Nevertheless, the cermet structure, with its large number of discontinuities, does not seem to be as able to retain helium as a one or two phase lithium-aluminum alloy. Also, an aluminum matrix cermet would be molten at maximum transient temperatures.

The other means of fabricating cermets are high energy forming and pressing and sintering. It is likely that these methods will be inferior to pressing and extrusion. In the first case, the costs would be much higher; in the second case, the product would be inferior and of lower density. Any of the three methods should be suitable for forming a Zr-2 lithium compound cermet.

The same deficiencies found in the SAP-lithium compound cermets will be found in the Zr-2-lithium compound cermets, with the exception that the Zr-2 cermet will be a solid at maximum transient temperatures. The biggest disadvantage of Zr-2 is its cost.

Cermets appear to offer no great advantages over the ceramics, even though the aluminum would serve to lower the vapor pressure of lithium, and the Zr-2 sould eliminate it completely at maximum transient temperature. The compounds that are proposed for use, outside of the $Li_2O \cdot 2SiO_2$, which will be used only if the transient does not exceed 1000° C, have acceptably low vapor pressures up to 1200° C. There would be little to gain by incorporating them in a cermet. Gas retention properties for a cermet during a maximum credible incident will be basically the same as those of the target material, since a large amount of gas from the target material would rupture the metal matrix. In addition, finely divided lithium compound particles might react with molten aluminum, liberating lithium. There do not appear to be any great benefits to be gained by going to a cermet material, though in the case of Zr-2 there would be no bad features to such a practice from a performance standpoint.

IV. EXTRACTION

A. General

The final step in the tritium production process is the extraction of the tritium from the target slugs. Extraction of the gas from a lithium-aluminum alloy target consists of heating the slug to drive off the He and T, followed by processing of the gas to separate out the tritium. While it is not necessary to melt the alloy to drive off the gas, this

[redacted]

is usually done. The mechanism of gas evolution depends largely on the He to expand and crack the material so that the tritium can escape. The tritium migrates from the solid solution α phase to the intermetallic LiAl β phase. Lithium tritide is formed and upon further heating goes off as tritium gas according to the reaction, $T + LiAl \rightarrow LiT + Al \xrightarrow{\Delta} LiAl + 1/2T_2$ (13). This exact reaction is not possible in the ceramic compounds, but the tritium will undoubtedly come off. If the helium is held in the lattice, and there are few voids available for it to coalesce in, gas extraction may be somewhat difficult. The behavior that makes these materials safe for use at maximum transient temperatures may make it necessary to go to extremely high extraction temperatures.

The three classes of materials become more difficult to extract as their stability in the reactor goes up. An important factor that could modify this type of behavior would be an unexpectedly high rate of gas evolution by some other mechanism that does not necessitate cracking of the target material. There is a possibility that something of this nature may be possible. This will be covered under the particular material.

B. Discussion

1. Lithium Silicates

The lithium silicates have some advantages over the aluminates and aluminosilicates. There are also some disadvantages. The silicates melt at lower temperatures than the other two classes and, on this basis, are easier to extract. The difficulty is that the silicates are highly corrosive. Container life would be very short. An alternative that would permit lower extraction temperatures and less container corrosion could consist of fluxing the silicate with an oxide to generate a low melting eutectic. However, it might be necessary to pulverize the target element in order to speed up such a reaction. By adding approximately 80 w/o $Na_2O \cdot 2SiO_2$ to the Li_2O SiO_2a eutectic with a melting point of 709° C can be produced. Similar gains may be made by adding appropriate quantities of $Na_2O \cdot 2SiO_2$ or $Na_2O \cdot SiO_2$ to $2Li_2O \cdot SiO_2$ or $Li_2O \cdot 2SiO_2$. Details of this are shown in Appendix III. It is also possible that the gas may be released by mechanical subdivision; possibly, subdivision would have to be followed or preceded by heating.

2. Lithium Aluminates

It may be extremely difficult to extract the gas from the lithium aluminates. The melting points are entirely too high to consider melting as a feasible method. It should be possible to find an oxide or mixture of oxides to flux these materials. Mechanical subdivision would probably be necessary, and might release a great deal of gas byitself. There is also a strong possibility that heat treatment followed by mechanical subdivision would work.

3. Lithium Aluminosilicates

The aluminosilicates will probably respond to the same techniques

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as the aluminates. Fluxing, heating, and mechanical subdivision can be combined to do the job. It will be easier to flux the aluminosilicates than the aluminates, and the melting temperatures of the former are not as high. The problems will be about the same, however.

4. Summary

In summary, it can be seen that the extraction properties of the lithium silicates, aluminates, and aluminosilicates leave much to be desired. Undoubtedly, extraction of the tritium burden can be accomplished. It may be necessary to resort to fluxing of the material, or to a combination of heating and grinding, or, possibly, all three. There is a need for experimental work to determine if the problem is as difficult as appears on the surface, and what the best method for solving it would be.

IV. SUMMARY

The properties of a number of lithium compounds have been reviewed with the purpose of choosing some that meet requirements for use in the N-Reactor. These requirements have been outlined for both normal operating conditions and the design maximum credible incident for N-Reactor. The potential target materials were examined in light of these requirements, and three classes of compounds selected because of their ability to meet these requirements. A more detailed analysis of these compounds; the lithium silicates, aluminates, and aluminosilicates, was made. The problems that might arise in their fabrication and in the subsequent separation of tritium were also mentioned, with some possible solutions to these problems outlined.

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TABLE I

Lithium Compounds

Compound	ρ g/cc	ρ Li^6 g/cc	ρ Li g/cc	Structure	mol. wt.
LiCl	2.068	.0218	.340	Cubic (NaCl)	42.40
LiBr	3.464	.0178	.277	Cubic (NaCl)	86.86
LiF	2.601	.0447	.696	Cubic (NaCl)	25.94
LiI	4.061	.0136	.212	Cubic (NaCl)	133.86
$LiNO_3$	2.38	.0152	.237		68.95
Li_2CO_3	2.111	.0256	.398		73.89
Li_3N	1.30	.0498	.775	Hexagonal	34.83
Li_2O	2.013	.0599	.931	FCC	29.88
$LiAlO_2$	2.55	.0172	.268	Rhombohedral (LT) Tetragonal (HT)	65.91
$LiAl_5O_8$	3.61	.00605	.094	Cubic (LT) Spinel (HT)	265.54
Li_2SiO_3	2.52	.0229	.356		89.94
Li_2TiO_3	~2.6	.0212	.330	Cubic (NaCl)	109.8
$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	~2.5	.00714	.111	Derivative quartz	372.3
$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	~2.5	.00894	.139	High quartz	252.1
$Li_2O \cdot 2SiO_2$	~2.5	.0150	.233		150.1
$2Li_2O \cdot SiO_2$	2.33	.0347	.540		119.90
$Li_2O \cdot B_2O_3$ ($LiBO_2$)	~2.2	.0197	.307		49.75
Li_2SO_4	2.22	.0180	.280		109.94
Li_2C_2	1.65	.0452	.0392		37.8
$LiSO_3F$	2.3 (?)	.0113	.00277		106
$LiGaN_2$	3.35	.0168	.0145		118.75
LiH	.78	.0508	.0441		7.95

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TABLE I (continued)

Lithium Compounds

Compound	ρ g/cc	ρLi^6 g/cc	ρLi g/cc	Structure	mol. wt.
Li_2MoO_4	2.3 (?)	.01035- .01556	.161 - .242	Tetragonal prisms	173.83
Li_2WO_4	(?)	(?)	(?)	Trigonal	261.8
Li_2GeO_3	3.53	.0118	.184	Monoclinic	134.48
LiOH	1.43	.0269	.418	Tetragonal	23.95
Li_3PO_4	2.54	.0296	.46	Rhombohedral	115.80
$Li_3Na_3(AlF^6)$	2.80	.0102	.158	Cubic	371.75

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TABLE II

Lithium Compounds

Compound	MP, °C	BP, °C	C cal/mole°C	Solubility
LiCl	614	1352	12.20	v soluble hygroscopic
LiBr	552	1310	-	v soluble
LiF	840	1681	2.59	insoluble
LiI	440	1171	-	v soluble
$LiNO_3$	254	-	26.65(210°C)	v soluble
Li_2CO_3	735	d 1200	23.28	moderately soluble
Li_3N	856	-	-	decomposes
Li_2O	1427	1527	24 (25°C) 8,892(200°C) 2,497(100°C)	hygroscopic soluble
$LiAlO_2$	1610	-	-	insoluble
$LiAl_5O_8$	1950	-	-	prob. insoluble
Li_2SiO_3	1201	-	-	decomposes in hot H_2O
Li_2TiO_3	1520-1564	-	-	unknown
$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	~1420	-	-	prob. less soluble than Li_2SiO_3
$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	~1390	-	-	prob. much less soluble than Li_2SiO_3
$Li_2O \cdot 2SiO_2$	~1033	-	-	prob. decomposes
$2Li_2O \cdot SiO_2$	1250	-	-	hot H_2O decomposes
$LiBO_2$	846	d 1200	-	possibly decomposes
Li_2SO_4	859	-	-	v soluble

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TABLE II (continued)

Lithium Compounds

Compound	MP, °C	BP, °C	C cal/mole °C	Solubility
Li_2C_2	decomposes		------	reacts
$LiSO_3F$	360	----	------	very soluble
$LiGaN_2$	800	----	----	decomposes
LiH	688		8,200 at 0° C 13,500 at 527° C	decomposes to LiOH + H_2(g)
Li_2MoO_4	705	-----	-------	hygroscopic
Li_2WO_4	742	-----	------	very soluble
Li_2GeO_3	1239	-----	------	slightly soluble
LiOH	450	925	1900	soluble
Li_3PO_4	837	-----	-----	slightly soluble
$Li_3Na_3 (A_1F_6)_2$	710	-----	-----	slightly soluble

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TABLE III

Lithium Compounds

Compound	Coeff. of linear Ex. α cm/cm	k	from elements ΔH, K cal/mole	ΔF° or S°
LiCl	-	-	-97.70	-91.9(ΔF°) (25° C) 13.9(ΔS°)
LiBr	-	-	-87.40	-80.7(27° C) (ΔF
LiF	-	-	-145.6	(ΔS°) 8.5 (25° C) (ΔF°)-138.7 (25° C
LiI	-	-	-65.0 or -72.5	(ΔF°)-66.8 (25° C)
$LiNO_3$	-	-	115.28	-
Li_2CO_3	-	-	-290.54	21.60(ΔS°)
Li_3N	-	-	-47.5	-
Li_2O	-	-	-142.4	(25° C)9.06(ΔS°) (25° C)-133.8
$LiAlO_2$	12.4×10^{-6} (25-1000° C)	-	-284.33	-269.49(ΔF°)
$LiAl_5O_8$	8.2×10^{-6} (25-1000° C)	-	-	-
Li_2SiO_3	-	-	376.7	-
Li_2TiO_3	-	-	-399.2(300° K) -396.1(1500° K)	(ΔF°) -377.7(300° K) -288.3(1500° K)
$LiO \cdot Al_2O_3 \cdot 4SiO_2$	$.9 \times 10^{-6}$ (0-1000° C)	-	-	-
$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	-6.5×10^{-6} (0-1000° C) -8.6×10^{-6} (0-600° C)	-	-	-
$Li_2O \cdot 2SiO_2$	-	-	-	-
$2Li_2O \cdot SiO_2$	-	-	-	-
$LiBO_2$	-	-	-	-
Li_2SO_4	-	-	342.8	-

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TABLE III (continued)

Lithium Compounds

Compound	Coeff. of linear Ex. α cm/cm	k	From the elements ΔH, K cal/mole	ΔF° or S°
Li_2C_2	------	---	-----	-----
$LiSO_3F$	------	---	-----	-----
$LiGaN_2$	------	---	-----	-----
LiH	------	---	21.34	(ΔS°) 5.9 cal/mole°C at 25°C
Li_2MoO_4	-----	---	-----	-----
Li_2WO_4	-----	---	-----	-----
Li_2GeO_3	-----	---	-----	-----
LiOH	-----	---	105.13	(ΔS°) 12.8 ca/mole°C
Li_3PO_4	-----	---	-----	-----
$Li_3Na_3\ (A_2F_6)_2$				

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TABLE IV

Vapor Pressures of Lithium Compounds

Compound	1mm	10mm	40mm	100mm	400mm	760mm	
			T° C				
LiCl	783	932	1045	1129	1290	1382	
LiBr	748	888	994	1076	1226	1310	
LiF	1047	1211	1333	1425	1591	1681	
LiI	723	841	927	993	1110	1171	
$LiNO_3$	-	-	-	-	-	-	
	1mm	4mm	15mm	32mm	63mm	760mm	
Li_2CO_3	610	723	810	888	965	1270	CO_2
Li_3N	-	-	-	-	-	-	
Li_2O	955	1056	1125	1174	1215	1300	
$LiAlO_2$	Lithia loss negligible at 800° C-1200° C; becomes appreciable 1400-1700° C						
$LiAl_5O_8$	Lithia vaporizes at 1700° C						
Li_2SiO_3	-	-	-	-	-	-	
Li_2TiO_3	-	-	-	-	-	-	
$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	-	-	-	-	-	-	
$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	-	-	-	-	-	-	
	1mm	10mm	40mm	100mm	760mm		
$Li_2O \cdot 2SiO_2$	-	-	-	-	-		
$2Li_2O \cdot SiO_2$	-	-	-	-	-		
$LiBO_2$	-	-	-	-	-		
Li_2SO_4	-	-	-	-	-		

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TABLE IV (continued)

Vapor Pressures of Lithium Compounds

Compound							
Li_2Cr	Dissociates to metallic lithium and graphite on heating.						
$LiSO_3F$							
$LiGaN_2$							
LiH T°C	0.07 mm(Hg) 500		27 mm(Hg) 680			760 mm(Hg) 850	
Li_2MoO_4	-		-			-	
Li_2GeO_3	-		-			-	
LiOH	H_2O pressure (mm Hg)	2	23	61	121	322	760
	T°C	520	610	670	724	812	924
Li_3PO_4	-		-			-	
$Li_3Na_3(Al F_6)_2$	-		-			-	

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TABLE V

Vapor Pressure of Lithium Oxide

Pressure of water Vapor on Lithium Oxide mmHg	Exposure time hours	Loss in weight %	Temperature °C
Evacuation	2.5	3.3	1000
10^{-8}	2.0	3.2	1000
10^{-4}	2.5	6.4	1000
10^{-2}	2.0	12.4	1000
10^{-2}	0.5	18.4	1000

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[redacted]

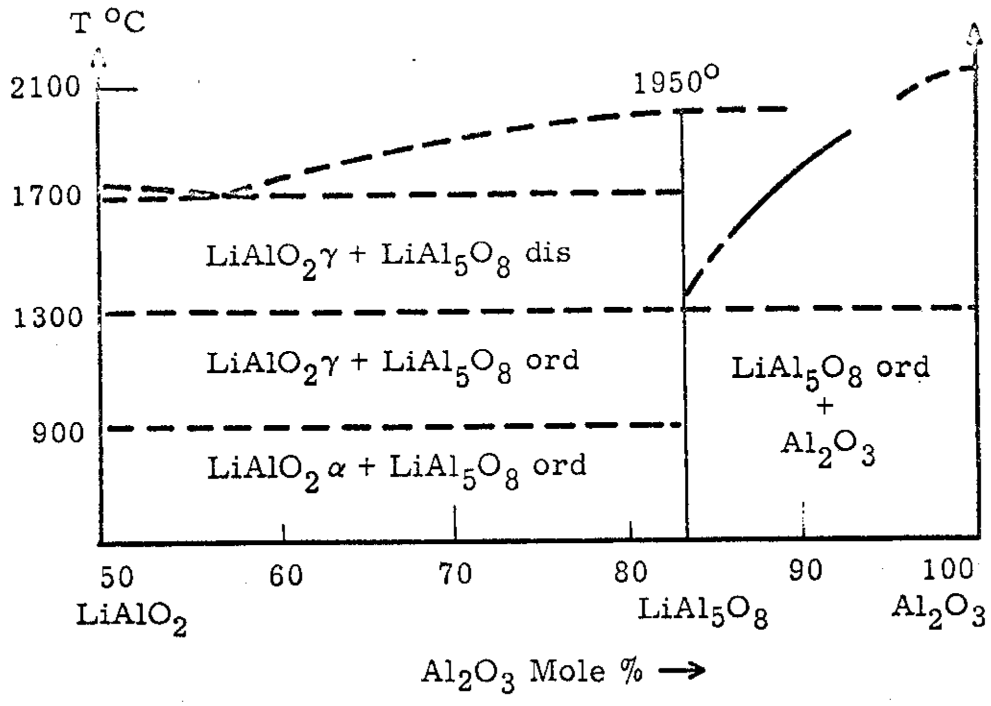

FIGURE I

$LiAlO_2$-Al_2O_3 Phase Diagram

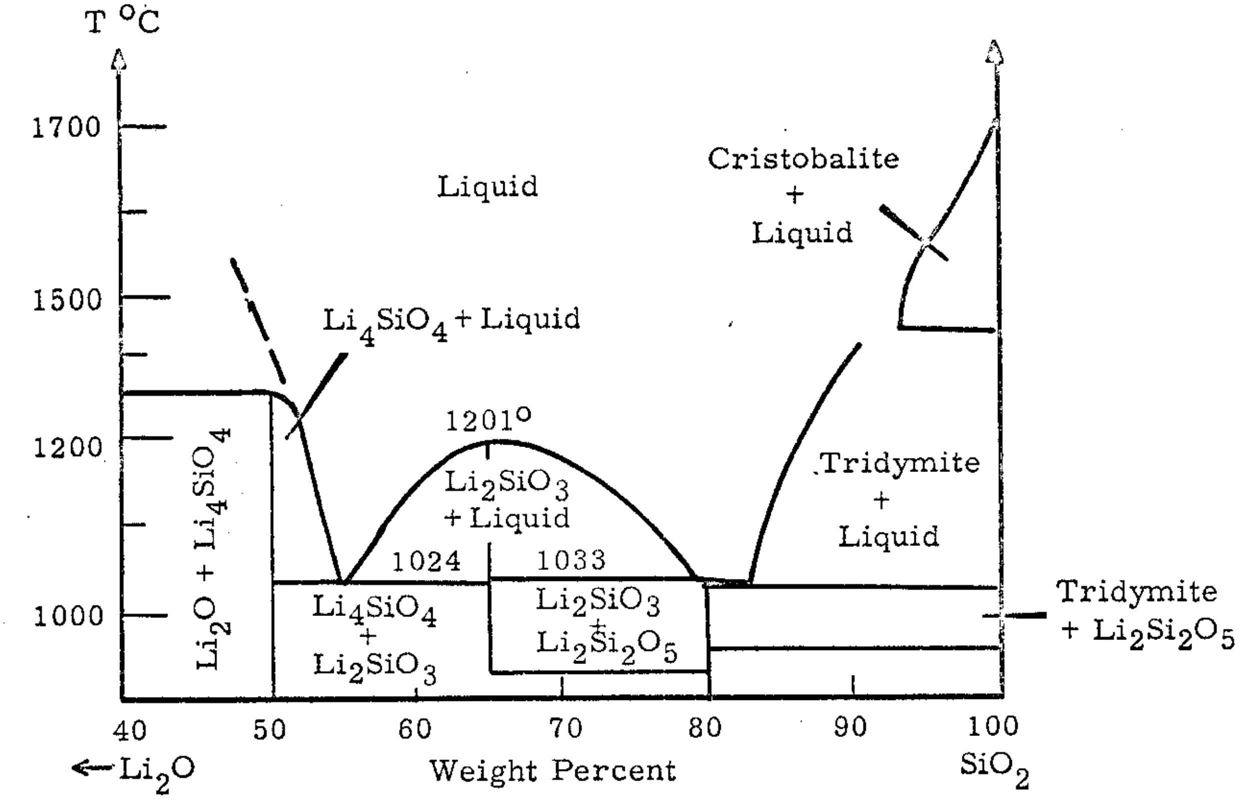

FIGURE II

SiO_2-$2Li_2O \cdot SiO_2$ Phase Diagram

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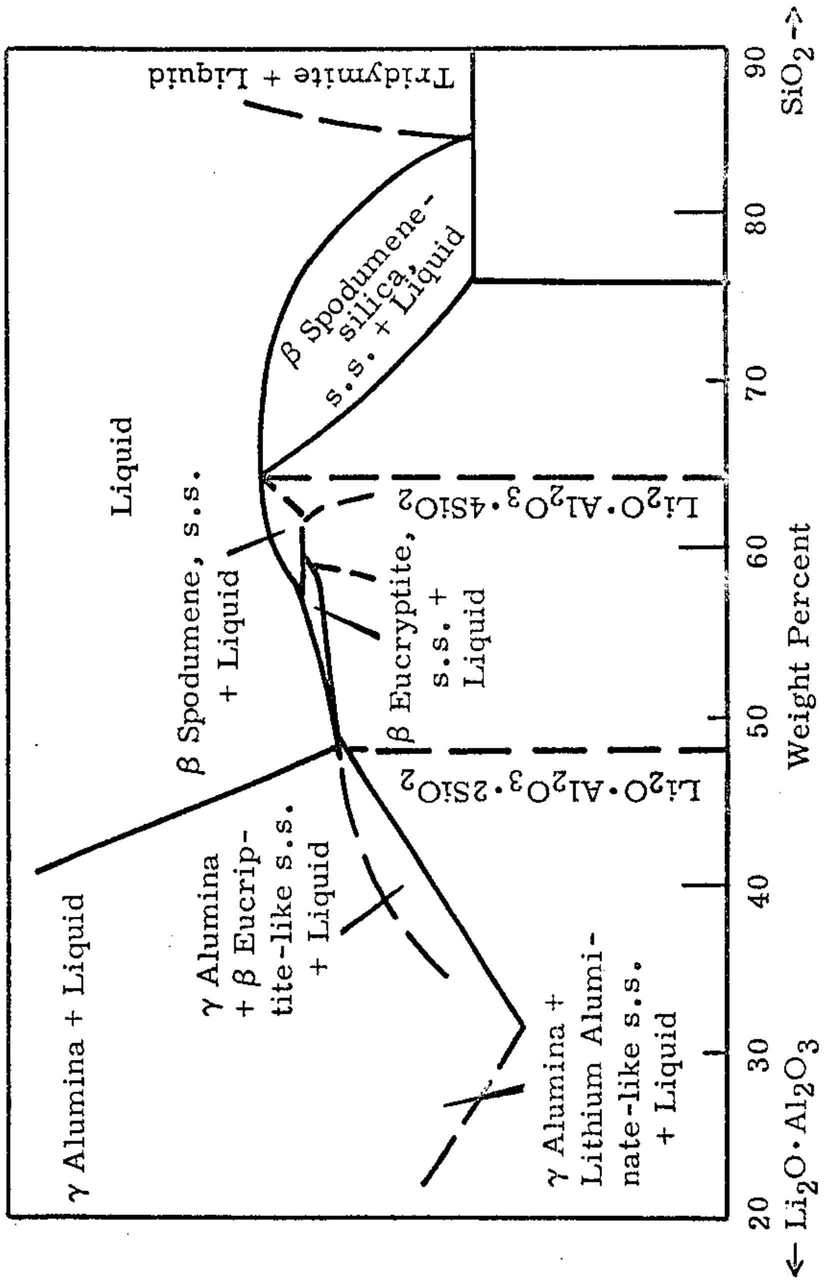

FIGURE III

SiO_2-$Li_2O \cdot Al_2O_3$ Phase Diagram

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Page 27

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APPENDIX I

(Thermal Expansion)
COMPATABILITY WITH ALUMINUM CAN AND Zr-2 CLADDING

I. The coefficient of linear expansion for aluminum is $24 \times 10^{-6°} C^{-1}$

II. The coefficients of linear expansion of the prospective target materials are all somewhat lower than that of Al.

$LiAlO_2$	12.4×10^{-6}/°C
$LiAl_5O_8$	8.2×10^{-6}/°C
$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	$.9 \times 10^{-6}$/°C
$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	-6.5×10^{-6}/°C (0-1000°C)
	-8.6×10^{-6}/°C (0-600°C)

III. The coefficient of linear expansion for Zr-2 is

6.5×10^{-6}/°C (0-700°C)

IV. The target tube has the following dimensions:

	ID	OD
Target material	-	.619"
Aluminum	.619"	.679"
Zr-2	.679"	.739"

V. The expansions on heating from 20°C to 300°C are given below:

Zr-2:

$$C = \pi d = .739\pi = 2.32''$$

$$\Delta C = \alpha C(\Delta T) = (6.5\times10^{-6})(2.32)(280) = 4.22\times10^{-3}{}''$$

$$\Delta d = .00422/\pi = .001343'' \; ; \; \Delta \ell = (24)(6.5\times10^{-6})(280) = .0437''$$

Al:

$$C = .679\pi = 2.135''$$

$$\Delta C = (2.135)(24.4\times10^{-6})(280) = 14.6\times10^{-3}{}''$$

$$\Delta d = .0146/\pi = .00464'' \; ; \; \Delta \ell = (24)(280)(24.4\times10^{-6}) = .1639''$$

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$LiAlO_2$:

$$\Delta l = l\alpha(\Delta T) = (24)(1.24\times10^{-5})(280)$$
$$\Delta l = .0833''$$
$$\Delta d = d\alpha(\Delta T) = (.619)(1.24\times10^{-5})(280)$$
$$\Delta d = .00215''$$

1) It appears that the aluminum can will be upset against the Zr-2 can since the yield strength of aluminum is ≈ 2,000 psi at 260°C and the yield strength of Zr-2 is 18,300 psi at 260°C.

2) The lithium aluminate will either fracture or densify, depending upon its state of aggregation, unless a gap is left to accommodate the expansion.

3) The other materials will be less likely to cause any problems since their expansion coefficients are either less than or about the same as the Zr-2 cladding.

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APPENDIX II

THERMAL SHOCK

FOR AN INFINITE cylinder of radius, r, THE THERMAL STRESSES ARE GIVEN BY:

SURFACE

$$\sigma_r = 0$$

$$\sigma_\theta = \sigma_z = \frac{E\alpha}{(1-\mu)}(T_A - T_S)$$

CENTER

$$\sigma_r = \frac{E\alpha}{2(1-\mu)}(T_A - T_C)$$

$$\sigma_\theta = \sigma_z = \frac{E\alpha}{2(1-\mu)}(T_A - T_C)$$

THE TEMPERATURE DIFFERENCE BETWEEN SURFACE AND CENTER WHEN THE CYLINDER IS COOLED AT A CONSTANT RATE IS:

$$T_C - T_S = \frac{.25\ b r^2}{k/\rho C_p}$$

T_C = center Temp.
T_S = SURFACE TEMP.
T_A = AVERAGE TEMP.

ASSUME: $\frac{T_C - T_S}{2} = T_A - T_S = T_C - T_A$

SURFACE

$$\sigma_\theta = \sigma_z = \frac{E\alpha(.125)\phi r^2}{(1-\mu)(k/\rho C_p)}$$

where $\phi = \frac{dT}{dt}$, °C/sec.

CENTER

$$\sigma_r = \frac{.0625\ E\alpha\phi r^2}{(1-\mu)(k/\rho C_p)}$$

$$\sigma_\theta = \sigma_z = \frac{.0625\ E\alpha\phi r^2}{(1-\mu)(k/\rho C_p)}$$

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ELASTIC MODULUS

THE ELASTIC MODULUS RANGES FROM 1×10^7 psi TO 3×10^7 psi FOR CERAMIC AND GLASSY MATERIALS.

COEFFICIENT OF THERMAL EXPANSION

THESE DATA ARE GIVEN IN TABLE III FOR SEVERAL COMPOUNDS.

THERMAL CONDUCTIVITY

THERMAL CONDUCTIVITIES RANGE FROM .004 (SODA GLASS) TO .036 ($MgAl_2O_4$ SPINEL) CAL/SEC/cm^2/°C/CM AT 100°C. AT 1000°C, THEY RANGE FROM .006 (SODA GLASS) TO .014 ($MgAl_2O_4$ SPINEL) CAL/SEC/CM^2/°C/CM.

SPECIFIC HEAT AND DENSITY

VALUES FOR THE SPECIFIC HEAT ARE LISTED FOR SEVERAL COMPOUNDS IN TABLES I AND II. IN GENERAL, THEY VARY FROM .20 cal/g/°C to .30 cal/g/°C.

STRENGTH

COMPRESSIVE:	20,000 psi to 60,000 psi
TENSILE:	5,000 psi to 15,000 psi

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CALCULATIONS

When a cylinder is cooled, the surface is placed in tension and the center in compression. The most dangerous stresses are at the surface. For a typical ceramic, making pessimistic assumptions, use the following expression to find the maximum permissable cooling rate.

$$\phi = \frac{8\sigma_T(1-\mu)\alpha}{E a r^2} \quad \text{where } \alpha = k/\rho C_p$$

$\rho = 2.5$ g/cm³ $C_p = .30$ cal/g/°C $k = .004$ cal/sec/cm²/°C/cm

$$\alpha = \frac{4\times10^{-3}}{(2.5)(.30)} = 5.34\times10^{-3} \text{ cm}^2/\text{sec.}$$

$$\alpha = 8.28\times10^{-4} \text{ in}^2/\text{sec.}$$

$\sigma_T = 5{,}000$ psi $E = 1\times10^{7}$ psi

$a = 12.4\times10^{-6}$ °C^{-1} $\mu = .2$

$$r^2 = (.375)^2 = .1407 \text{ in}^2$$

$$\phi = \frac{(8)(5\times10^3)(.8)(8.28)(10^{-4})}{(10^7)(1.24\times10^{-5})(1.407)(10^{-1})} = 1.519 \text{ °C/sec.}$$

For LiAlO$_2$:

$\sigma_T = 10{,}000$ psi $k = .036$ cal/sec/cm²/°C/cm

$a = 12.4\times10^{-6}$ °C^{-1} $\rho = 2.55$ g/cm³

$\mu = .2$ $C_p = .25$ cal/g/°C

$E = 2.5\times10^{7}$ psi $\alpha = 5.62\times10^{-2}\ \frac{\text{cm}^2}{\text{sec}} = 8.78\times10^{-3}\ \frac{\text{in}^2}{\text{sec.}}$

$$\phi = \frac{(8)(10^4)(.8)(8.78)(10^{-3})}{(2.5\times10^7)(1.24\times10^{-5})(1.407\times10^{-1})} = 12.9 \text{ °C/sec.}$$

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APPENDIX III

A. To produce a eutectic with a melting temperature of 847°C from $Li_2O.SiO_2$, the mixture composition must be as follows:

38 w/o $Li_2O.Si\ O_2$

62 w/o $Na_2O.SiO_2$

Therefore, to 100 g of $Li_2O.SiO_2$ add 163 of g of $Na_2O.SiO_2$.

B. For a eutectic with a melting temperature of 709°C the composition is found to be:

20 w/o $Li_2O.SiO_2$

80 w/o $Na_2O.SiO_2$

Add 400 g of $Na_2O.SiO_2$ to 100 g of $Li_2O.SiO_2$.

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