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THERMIONIC TECHNOLOGY PROGRAM A: INSULATOR TEST & EVALUATION

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by

Jesse C. Dobson
Tony Witt

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by

RASOR ASSOCIATES, INC.
253 Humboldt Court
Sunnyvale, CA 94089

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SUMMARY

The Thermionic Technology Program (TTP) consisted of two major efforts, 1) evaluation of insulators and 2) evaluation of thermionic converters. This report details the work performed on the insulator phase of the program.

Efforts were made to better understand the mechanisms involved in the electrochemistry of insulators at elevated temperatures by modelling the ionic transport through the various layers of the insulator package. Although rigorous analytic solutions could not be obtained owing to a lack of detailed data, a simplified model indicated that alumina should not fail by depletion of aluminum for thousands of years, whereas calculations for yttria revealed a far more rapid depletion of oxygen and consequently earlier failure.

Methods for microscopic and electrical testing of cylindrical insulator samples were developed, and an improved test oven design was initiated. Testing of alumina/niobium cermet samples revealed rapid failure contrary to the theoretical predictions for alumina. Large discrepancies in the initial conduction activation energy amongst the various samples suggested that different mechanisms could have controlled the conduction and hence the failure in different samples although all had undergone nominally identical processing. The short lifetimes reveal how rapidly ambient conditions in thermionic power conversion can degrade the performance of insulating oxides. It was concluded that minor dopants could have been responsible for the early breakdowns. Thus, high purity materials with precise quality control will be necessary for trilayer package development.

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1.0 INTRODUCTION

The formation of the Strategic Defense Initiative (SDI) has triggered a requirement for larger electric space power systems in the multimegawatt regime. However, mid-power (<1 MWe) requirements still remain, and thermionic fueled element (TFE) technology can fill this need. Thermionic energy conversion for nuclear reactor space power system affords the following advantages:

- o Low mass and volume in orbit.
- o Readily scaleable over the energy range from 0.1MWe to several megawatts.
- o High reliability with few moving parts.
- o High survivability, a consequence of in-core power conversion and high temperature radiator.

This thermionic technology program (TTP) addressed certain key issues relative to TFE development. This volume, Volume I, of the two reports deals with the sheath insulators that electrically isolates the emitter and collector. Volume II addresses techniques to enhance converter performance while still gleaning valuable fundamental information.

Sheath insulators in the TFE configuration serve two vital functions. First, they must isolate the emitter from the collector to avoid an electrical short circuit through the liquid metal coolant. Second, they must conduct heat from the collector to this coolant. Material requirements for these two conditions seem mutually incompatible. Materials with high electrical resistivity typically exhibit low thermal conductance and vice versa. Thus, there is not a clear cut solution. This challenge has taxed the engineer to come up with acceptable alternatives. The approach has been first to design insulators as thin as possible thus maximizing their thermal conductance. Secondly, alternative methods to increase overall conductance are being

developed. Additionally, the insulator must withstand thermal stresses and temperature gradients. Metal oxides serve as a reasonable compromise for insulator materials. They provide most of the required physical properties plus they can be brazed to the solid components of the system.

Three alternative concepts have been considered. These are identified as trilayers, graded, and cermet. A trilayer fabrication is one where the cross-section of the cylindrical insulator is made up of three distinct layers. The middle lamina exhibits excellent electrical resistance properties while the two exterior laminas have high thermal conductance and facilitate bonding to other components. Graded insulators are a modern-day analogy to the trilayer. These insulators are formed by plasma spraying mixtures of ceramic and niobium, but the percentage of each varies in a programmed fashion throughout the wall thickness to yield the final product. Thirdly, cermet insulators have been developed where niobium microspheres are dispersed within sintered ceramic. The mixed materials are compressed and fused into the designed cylindrical shape.

Added to the other technical complications, the insulator must survive seven years of service within the reactor. In order to do this, the insulator must be produced from a limited selection of acceptable materials. An additional technical complication for insulator design to overcome is broadly referred to as electrolysis. Molecules at high temperature become more active. Superimpose on this situation, a high direct current voltage. The combination of the two causes a migration of the atoms that make up the oxide insulator with the oxygen moving to the cathode and the metal ions migrating to the anode. The net result is a continuous breakdown of the insulator. The problem is exacerbated by both increased temperature and voltage.

Although sheath insulators have survived thousands of hours in core, post test examinations have revealed problems. Examinations have revealed delamination of trilayers and breakdown of insulators probably caused by electrolysis. Thus, improved insulators continue to demand attention.

The cermet insulators tested in this program were produced by Thermo Electron Corporation. The reader is referred to their final report for details of the fabrication. This report covers the test procedure and examines the results. It also develops the theory for examining the electrolysis phenomenon.

2.0 EXPERIMENTAL APPROACH

The primary experimental goal of this out-of-core project was to examine the effects of long term exposure of insulators to high temperatures (>1100 K) and moderately high electric fields (~ 1000 V/cm). In order to determine the changes in the insulator packages caused by testing under these conditions, it is essential to thoroughly characterize the sample prior to and following testing. This characterization must include both microstructure evaluation and electrical behavior. Quantities of interest are the electrical conductivity as a function of temperature, grain size distribution, impurity/dopant distribution, and porosity. Because the test samples include niobium cermets, the size and distribution of niobium in the ceramic matrix is also important and therefore of interest.

The conductivities can easily be determined using the test stand/oven assembly by applying a fixed voltage and monitoring the resulting currents. The other properties are usually estimated by first cutting and polishing the material to a <1 micron finish, etching to show the grain boundaries and analyzing the resulting microstructure using either an optical or electron microscope and various surface analytical techniques. After this analysis, the samples can be life tested. The samples are exposed to temperature and electrical field and the resistance is monitored for long term changes. If the test specimen loses its resistivity, its microstructure can be reexamined in an attempt to elucidate the cause of that failure.

In previous programs, testing of sheath insulator assemblies has been conducted in isothermal ovens, since this greatly facilitated the uniform heating of many samples at one time and attaching of electrical leads to the samples. However, this method had come under question owing to the problem referred to as thermal runaway. Thermal runaway occurs when a localized reduction in resistance exists, as is often the situation in an insulator. This decrease in resistance creates a local temperature rise due to increased Joule heating from the electric current which in turn leads to further reduction in resistance. This cycle continues in a runaway situation until

the sample eventually fails. Thermal runaway is the most common failure mechanism in the low to moderate electric fields used in thermionic converters (generally <500 V/cm). For the purpose of these tests, it was felt that it was very important to develop a test oven that would alleviate this problem. The design of a temperature gradient oven allowing greater heat dissipation should be a major advance toward that goal.

3.0 EQUIPMENT AND PROCEDURES

3.1 METHODS

Microstructural Evaluation

Microstructural evaluation was begun by polishing test samples. However, differences in hardness between niobium and Al_2O_3 caused considerable difficulty in obtaining a smooth surface finish by mechanical polishing, especially near ceramic-metal interfaces. Such interfaces occur in the test samples both at the cladding edge and within the cermet, so it was very important to obtain a high quality of polish in these regions. This difficulty was overcome by using a chemical-mechanical polishing technique developed in conjunction with Beuhler, Ltd. The initial steps involved grinding on various grits of SiC paper and polishing with diamond paste. The key final polish utilized 0.3 micron Al_2O_3 powder in a mixture of distilled water with 3% H_2O_2 at slow rotation speeds. This made smooth polishing of the niobium possible.

Samples were etched in an aqueous solution of HNO_3 and HF to expose the grain boundary structure in the niobium following polishing. The niobium regions were then examined microscopically for grain size and general features. After examination of the niobium, the samples could be prepared for microscopic examination of the Al_2O_3 region. In order to expose the grain structure in the alumina, it was necessary to further etch the material by boiling it for ~10 minutes in H_3PO_4 . This step had to be performed after the grain size distribution of the niobium was recorded, since the niobium is severely attacked by the acid.

Resistance Evaluation

The electrical resistance of multiple cylindrical samples was measured by stacking the samples along the axis of the chamber in an isothermal oven. This stack of samples was located in the center of a helical heater winding. Up to six samples are held a fixed distance from the heater (and each other) by niobium spacer rings. These spacers also acted as the common ground to the

inner electrodes of the cylindrical samples. Leads were attached to the sample bodies, guard-rings and spacers by twisting niobium wire into grooves or by spot welding. These leads were brought out of the oven to the data acquisition equipment through vacuum feedthroughs. Voltages were applied to the exterior electrodes (guard rings and body) by external DC power supplies. Sample temperatures were measured by means of W/W-5% Re thermocouples fixed to the spacer rings at the top and bottom of the stack of samples. The oven temperature was held constant to within approximately five degrees Celsius by fixing the power to the oven element with a Variac.

The resistance of each sample was calculated using the current values measured with a picoameter. When the current became too high (sample resistance too low) for the picoameter, the currents were determined by measuring the voltage across a known (relatively small) resistance in series with the sample. The ammeter was felt to be more accurate (especially at low current levels), so it was utilized for current measurement as much as possible. Knowing the applied voltage and the current through each sample, the sample resistances could be easily calculated. These data were taken every minute and recorded to a disk once an hour, unless the resistance of the sample was changing rapidly. The system continuously calculated the rate of change of the resistance and recorded data to a disk at a frequency related to this rate of change to a maximum of once per minute. This was done to increase the resolution of the change in resistance during failure episodes, which may help determine the failure mechanism(s).

The samples were heated under vacuum and allowed to outgas for several hours. The chamber was then back-filled with a few torr of high purity helium. At the test temperature, the electrical resistance was measured by applying 1 volt DC. The temperature was then decreased in 50°C increments and the resistance measured upon stabilization at each temperature. These data allowed the determination of the activation energy of the process(es) controlling the resistivity under the experimental conditions. The samples were then brought up to the experimental temperature. The experimental voltage was then applied continuously, and the resistances were monitored as described above.

3.2 EQUIPMENT

As discussed previously, thermal runaway is a frequent undesired failure mode in insulators. Because of the need to avoid this phenomenon, a major effort toward a better experimental oven design was set as a goal for this task. It was thought that if there were a considerable heat flux through the sample, as there is in a thermionic converter (generally $>10 \text{ W/cm}^2$), then the localized heating can be reduced by improved heat dissipation. This was the rationale behind development of a thermal-gradient oven design.

The initial design conceived for the oven consisted of a central heater made of tungsten wire embedded in ceramic, which would radiate to the samples. Quick calculation of the radiant heat losses, however, showed that to have a heat flux of even 1 W/cm^2 would require an unacceptably high temperature for the heater. After surveying the alternatives, it was decided to use a low pressure of an inert gas (~ 10 Torr helium) to provide heat conduction. This allowed a heat flux of $\sim 10 \text{ W/cm}^2$ with a temperature drop of $<100 \text{ K}$ across the gap from the heater to the sample. This choice was recognized as non-ideal but was deemed to be the better alternative when compared with an unacceptably low heat flux or solid heat conduction.

The initial heater design failed, however, due to a break in the wire caused by solid-state reaction with the alumina tube at the 1600 K operating temperature. The high temperature resulted from the temperature drop within the ceramic. Replacing the tungsten with niobium aided but did not solve this problem. Two alternative designs were developed. One approach utilized a grooved alumina tube with a helix of niobium wire wrapped on the outside of the ceramic which would lower the wire temperature. The other consisted of a thin-walled molybdenum tube encased in an alumina insulating sheath. Both designs gave good performance during accelerated life (high temperature) testing. The thin-walled tube had a better temperature distribution along its length. This design was also inherently more rugged than the wrapped design. Therefore, it was chosen as the heater design for the ovens.

A drawing of the heater design is shown in Fig. 3.2-1. The current used to heat the tube was returned along the molybdenum rod running coaxially in

Fig. 3.2.1 Molybdenum heater for temperature gradient oven

the center of the tube. This rod became significantly hotter than the wall of the tube, which helped even out the temperature distribution along the tube. A typical plot of temperature versus tube length is shown in Fig. 3.2-2. The difference in temperature between the center rod and the tube wall caused a mismatch in thermal expansion, however, so the current attachment for the center rod had to be free standing to prevent bending of the heater. The overall heater and sample chamber design is shown on Fig. 3.2-3. A detailed diagram of the sample/spacer configuration is seen in Fig. 3.2-4. Heat was conducted to the water-cooled jacket by the low pressure helium. Contaminants in the helium were minimized by the titanium sponges at the top and bottom of each heater. Spraying from the titanium, which was unexpected, was prevented from contaminating the samples by thin niobium shields.

The sample chamber setup for the isothermal oven was very similar to that illustrated in Fig. 3.2-3. The only difference was the heater. Instead of the samples surrounding the heater, the heater surrounded the samples. In the isothermal oven, the heater was a large diameter helix of wire that was placed around the sample stack. The helix was heated directly by passing the current through it with the heat radiating to the samples. Due to the runaway problem, it was hoped to avoid the use of this oven design as much as possible; but time constraints forced its use for testing prior to optimization of the gradient oven design.

Fig. 3.2-2 Temperature profile along length of heater

Fig. 3.2-3 Overall oven design with samples in place

Fig. 3.2-4 Detail of sample/spacer geometry

3.3 DATA ACQUISITION SYSTEM

As noted earlier, thousands of data points were collected and filed. Taking and entering these data by hand would not be practical. The decision was made at the outset to provide an automatic data acquisition system that would perform the large majority of measurement, display, and storage functions.

Prior experience at RAI has included the data acquisition system assembled for the SP100 experiment, which has been running almost continuously at GA Technologies since January, 1985. The TTP data acquisition resembles the SP100 system in many aspects, using the same Hewlett-Packard 200 series computer and some of the same software modules. In other aspects, however, the new system is distinct. Most notably, the software is designed to make the device highly versatile and to allow convenient configuration to many types of experiments; additionally, the new system includes a more sophisticated data logger and the capability to measure, display and file J-V curves. For the TTP program, the software is configured to allow convenient viewing of temperatures and other insulator control parameters relevant to test performance.

Hardware

The data acquisition system is assembled from the following components: the computer and peripherals, the data logger, and the digital electrometer. These are all housed in a "roll-around 43" relay rack cabinet.

The heart of the data acquisition system is the Hewlett-Packard 9826 desktop controller. It is a 16-bit Motorola 68000 based unit operating in the HP "Rocky Mountain" BASIC language system. This language is particularly attractive for operating external instruments because of the convenience and flexibility with which input/output operations can be performed over the IEEE-488 parallel interface bus. All peripherals, the electrometer, and the data logger communicate with the computer over this bus.

The 9826 is a single box with a built-in keyboard, 50 column monitor, and a 5.25" floppy drive. The backplane has eight expansion slots, two of which are used to expand the system RAM to 1.25 Mbytes.

A dual 3.5" floppy drive unit is used in conjunction with this computer because of the convenience of this media format and to provide compatibility with other RAI hardware. A Hewlett-Packard 2225A inkjet printer is used to make hard copies of data displays.

The sample currents are measured by a Keithley 617 electrometer. This is a digital auto-ranging device with 10^{-15} amp sensitivity. The data are transmitted to the HP controller over the IEEE-488 bus. The electrometer has a maximum input of 20 mA which is equivalent to a 1000 ohm sample with 20 VDC applied. At lower resistance (higher current) the electrometer is not viable, and the current must be measured as the voltage drop across a standard resistor in series with the sample. This voltage can be measured directly by the data logger. --The switchover from the electrometer to the resistor is done manually.

The ~~last major hardware component~~ is the Hewlett-Packard 3497A data logger. This unit consists of a digital multimeter (DMM), five slots for accessories (20 channel multiplexer cards, counter, actuator card, etc.,) and a microprocessor controller/buffer. The data logger receives an instruction message from the host computer, makes the appropriate measurements, stores the data in a buffer, and sends the data to the computer when requested to do so. Minimal time is spent supervising the data logger because it does not require instructions from the computer to coordinate channel closing and data taking, the computer is freed up for interactive use with the operator.

Software

At the start of program execution, a series of data files are read which configure the program. These files include information such as which subroutines to use to convert voltmeter readings for each parameter to the

appropriate real unit (e.g., degrees Kelvin or amperes), what axes to use for plotting time histories of the data, and the location of each parameter on the data display screens. Upper and lower setpoints for each parameter are read as well. An interactive routine is then called to set the internal computer clock.

Once the program is initialized, the computer instructs the data logger to make voltmeter readings of all multiplexer channels once a minute. The instruction is sent a few seconds before the even minute, so that the data from the buffer can be read by the computer on the even minute. The voltage measurements (e.g. temperatures) are measured directly by the DMM of the data logger. The data logger is used indirectly to measure currents. This device closes actuators which put the electrometer in series with the sample allowing it to measure the current. Different actuators sequentially switch the electrometer to each body and guard ring circuit until all samples have been scanned. Measuring the currents through four sample bodies and guard-rings takes approximately forty seconds. This long scan period is largely due to use of the auto-ranging feature of the electrometer. The voltmeter readings are then converted to units of voltage, current, temperature, etc., according to the configuration schedule.

The converted data are then stored in appropriate arrays and displayed on screen. All data are kept in memory for eight hours before it is overwritten, and data taken on the hour are kept in memory for one week before it is overwritten. This allows stripcharts to be plotted on screen without addressing mass storage media. The hourly data are always written to the "data" disk, and the minutely data are written to an "error" disk when the values are changing rapidly. Each datum is checked against its upper and lower setpoint. If the value is outside the prescribed limits, the printout on the screen is high-lighted as an alarm. The time required for these data handling routines is about three seconds; for the remaining time, the computer is free for interactive use.

Time histories for any parameter can be obtained by selecting the "Stripchart" key. A simple selector routine allows the operator to choose any of the parameters on the viewed screen. Timebase choices are: previous two hours, eight hours, and one week. A graphics routine plots the data on axes determined by the configuration data files. These time histories are particularly useful for determining what conditions may have led to an event of anomalous behavior. If desired, a hard copy of the time history can be printed.

4.0 RESULTS AND EVALUATION

4.1 PRE-LIFE TEST EVALUATION

Microstructure

Al_2O_3 -Nb cermet samples were fabricated by ThermoElectron Corporation. These samples contained 2% Y_2O_3 as an additive to the alumina. One sample was prepared for microscopic examination as previously described. The resulting microstructure of the insulator package is shown in Fig. 4.1-1a. The grain size in the niobium ranges from about 40 to 400 microns. This is sufficiently large that the effect of grain boundary transport should be negligible due to the low grain boundary area per unit volume of the material. The inner layer of the niobium exhibits a larger degree of pitting and sharper grain boundary definition than the outer layer, possibly due to a higher content of an impurity, e.g. oxygen. An expanded micrograph of the cermet layer (Fig. 4.1-1b) shows a fair amount of porosity in the alumina layer. Part of this apparent porosity, however, may actually be pullout of the niobium spheres from the ceramic matrix which can occur during polishing processes.

The grain structure of the alumina was much finer than that of the niobium, with grain size ranging from <0.5 to about 2.0 microns (Fig. 4.1-2). Due to the inclusion of 2% Y_2O_3 in the ceramic, a considerable amount of a second phase, which analyzed to be $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), was found in small precipitates between grain boundaries. This second phase can be seen in the TEM micrograph of Fig. 4.1-3. Orientation and distribution of these precipitates suggest that the alumina grains are surrounded by a thin coating of this phase. EDAX analyses of the YAG phase showed a niobium concentration of 3-3.5 atom %, while none was detected in the alumina grains. This indicates that a reaction between the niobium and the YAG occurred, probably during hot isostatic pressing with niobium diffusing along the grain boundaries to the precipitates. There was no evidence of greater niobium concentrations in the precipitates near the niobium spheres. This could mean that some sort of equilibrium concentration of niobium in YAG at the HIP conditions was reached.

Figure 1a. Polished cross-section of Al₂O₃
cermet sheath insulator. 56 X

Figure 1b. Expanded micrograph of cermet region
of insulator package. 213 X

Figure 2 - Scanning electron micrograph of alumina region of the cermet.

Figure 3 - Transmission electron micrograph of Al₂O₃ showing second phase at grain boundaries.

The presence of this second phase on the grain boundaries could greatly affect the electrical properties, and it was vital that its presence prior to life testing be known.

Temperature - Resistance Relationships

Electrical resistance as a function of temperature for four Al_2O_3 -2% Y_2O_3 niobium cermet samples was measured. These data are shown in Fig. 4.1-4. As can be seen from the data, the activation energies for samples 1-36-5 and 1-36-3 have similar values (~8.5 kJ/mole). Although their activation energies are very similar, the origin of the factor of 30 difference in the absolute resistances of these two samples is unknown. The other two samples yielded data that were not smooth, so it was difficult to determine an activation energy. The estimated value was ~87 kJ/mole. These values are consistent with those found by some investigators for polycrystalline Al_2O_3 (1) but would generally be considered low. It is possible that some mechanism other than conduction through Al_2O_3 is controlling the resistivity here, perhaps conduction through the surface films that became evident for these samples (2) or conduction in the YAG phase. From the extreme difference in the activation energies of the two pairs of samples, it seems probable that a different mechanism is controlling the conduction in each type. As will be shown in Section 4.2 the latter two samples had inferior life performance to the former two samples.

Another observation during these tests was that the current used to calculate the resistance drifted with time. This was attributed to the equilibration of the sample with the test environment. Minimizing this drift was the goal of heating the sample to test temperature prior to resistance measurements, and this approach was fairly successful, although it was necessary to wait ~12 hours after the temperature had stabilized to obtain stable current measurements.

4.2 LIFE TESTING

The work statement for insulators tests called for life testing of six each of the following cermet insulator packages supplied by TE: 1) Al_2O_3 and 2) YAG. The geometry of the samples is shown in Fig. 4.2-1. Guard-rings

Fig. 4.1-4 Determination of activation energies for conduction in Al_2O_3 -2% Y_2O_3 cermet.

Fig. 4.2.-1 Sheath insulator configuration

were included to prevent leakage currents from masking the resistance data. Because the Al_2O_3 samples were received prior to the completion of the improved oven described in Section 3.2, it was decided to test only four of these in the isothermal ovens that had been used for the SP-100 thermionic program. Holding back two of the samples would allow comparison of the isothermal oven results with those obtained using the new oven. The four samples were life tested according to the matrix described in Table 4.2-1.

TABLE 4.2-1
Life Test Matrix for Al_2O_3 Cermet Insulator Packages

<u>Sample #</u>	<u>Applied Voltage</u>	<u>Temperature (K)</u>
1-24-1	30	1250
1-24-2	30	1250
1-36-3	50	1100
1-36-5	10	1400

These conditions were chosen to give one duplication of data and to test the extremes of temperature and applied voltage. Unfortunately, it appears that sample variation played a more dominant role in determining insulator lifetime than experimental conditions. The voltage was applied using three direct current voltage supplies, at 10, 20 and 50 volts respectively. The 10 and 20 volt supplies were placed in series for the 30 volt supply. Data for the temperature, applied voltage and current were recorded every 15 minutes. Samples were considered to fail when the resistivity decreased to less than 4×10^4 ohm cm. This resistivity value is considered the approximate lower limit for use in a thermionic converter. Lower resistance would lead to unacceptable power loss due to leakage currents. Current readings were converted to resistivity according to the formula:

$$\rho = \frac{V \pi (d_1 + d_2) L}{i (d_1 - d_2)}$$

- V = applied voltage
i = measured current
L = sample length
d₁ = outside diameter of insulator
d₂ = inside diameter of insulator

All four samples failed (i.e., the resistance dropped below 200 ohms) in less than seven days on test. These seven days also contained long periods of upset in experimental conditions. All failures of the samples were very sudden, going from high to very low resistances in less than one hour.

The resistivity data for sample 1-24-1 is shown in Figure 4.2-2a. The accompanying temperature and voltage histories are shown in Fig. 4.2-2b and c respectively. The applied potential for all samples was at 10 volts for the first 24 hours due to operator error. The temperature was also only 1200 K for most of this period. The resistivity of the sample tracks as expected with variations in temperature. Simultaneously with the increase in voltage, the resistivity dropped suddenly over an order of magnitude, where it stabilized for approximately 6 hours. At this point the current increased (the resistivity dropped) suddenly to a value in excess of the protecting fuse. Thus, the resistivity is shown to increase, since the circuit was opened. Attempts to replace the fuse with a larger one only led to quick failure due to excess current, meaning the sample's resistance was very low. The samples were not removed immediately to prevent further interruption of the experiments. The resistance of this sample at room temperature was then <1 ohm. Attempts were made to remove any surface films that may have existed on the ends of the samples or in the guard rings, but the resistance remained very low.

Since sample 1-24-2 was in the same oven, its test history is the same as 1-24-1. The resistivity changes were remarkably similar, also, as shown in Fig. 4.2-3. The major difference was that the failure of this sample occurred

Fig.4.2-2a Resistivity of sample 1-24-1
through life test.

Fig. 4.2-2b Temperature history of sample 1-24-1

Fig 4.2-2c Applied voltage on sample 1-24-1

Fig 4.2-3 Life-test resistivity of sample 1-24-2

three hours prior to its counterpart. Attempts to restore the resistivity by removal of surface films failed for this sample, too.

The results at higher potential and lower temperature (sample 1-36-3) were more promising. The data are shown in Fig. 4.2-4. This sample was raised to its test voltage of 50 V after 26 hours on test, which caused the resistivity to become slightly unstable, whereas it had been very steady while only 10 volts were applied. The resistivity was beginning to rise, possibly due to polarization at the interfaces, when the loss of temperature was accompanied by a decrease in the measured resistance. This result is certainly unexpected. The restoration of temperature caused little change in resistivity, and the guard rings on this sample failed after ~120 hours on test.

Sample 1-36-5 was operated at low voltage and high temperature and also yielded superior results to those tested at median conditions. The resistivity was very stable for the first day but fluctuated noticeably during the second (Fig 4.2-5). Temperature and power were lost for about three days in the middle of the test period. The very high resistivity of the sample dropped as the temperature was restored. Continued operation at temperature resulted in a sudden decline in resistivity and eventual failure after ~24 hours.

After either the body or the guard rings had failed on all of the samples, the tests were terminated for failure analysis. The samples were submerged in freon, and a voltage was applied to them. If the low resistance(s) was localized, the freon should boil in the vicinity of the short. This was the case for several of the insulators, but removal of the surface layers and plasma sprayed layer in these areas did not result in an increase in the resistance of the sample. Therefore, conduction on external surfaces was not considered to be a likely failure mechanism for these samples.

Before further testing of these and the other two samples was to begin, TE reported the finding of a conductive surface layer that formed on these cermets at temperature in the presence of an electric field. The layer seemed

Fig. 4.2-4 Resistivity of sample 1-36-3

Fig. 4.2-5 Resistivity of sample 1-36-5

to be associated either with the YAG phase that formed by reaction of the Al_2O_3 with the Y_2O_3 additive or contamination from diffusion pump oil. Due to this finding, further testing of these cermets was deemed unproductive; and the experiments were discontinued. No additional samples were received from TE so no further life studies could be performed.

The results of the life tests were not promising, but some useful information can be seen in the limited results. The large discrepancy in activation energy amongst the samples suggested that different mechanisms controlled the conduction in samples that had undergone supposedly identical processing. This effect illustrates the sensitivity of the electrical properties of these materials underscoring the importance of quality control during manufacture. If the true behavior of these materials is to be studied, it is imperative that high quality, consistent processing be developed. This development is absolutely vital for utilization of these materials in real thermionic devices.

The short lifetimes seen for these samples, while perhaps not indicative of the intrinsic properties of the insulating material, are a good example of the rapidity with which the ambient conditions of thermionic power conversion can degrade the performance of insulating oxides. Due to the limited results and untimely termination of the life testing, a major effort toward modelling the lifetime of the insulators was made by examination of the mass transport behavior in the trilayer package. The progress on this effort will be examined in Section 5.

4.3 ULTRASOUND FOR NON-DESTRUCTIVE EVALUATION OF INSULATOR PACKAGES

The purpose of this subtask was to investigate the usefulness of an ultrasonic technique for the non-destructive evaluation (NDE) of insulator packages, both as a quality assurance method in manufacturing and as an in situ method of detecting failure during life testing. The usefulness of the former is obvious, and it was felt that the latter would provide further insight into the failure mechanisms that occur during simulated operation. To this end, samples were sent to two groups involved in the industrial application of this technology to make preliminary estimates of the effectiveness of

this approach for the following uses: 1) detecting cracks in the ceramic phase, 2) detecting failure of the bond at the ceramic niobium interface, 3) measuring the thicknesses of each layer and 4) determining the size and spatial distribution of the niobium inclusions in the ceramic phase. It was desired to make the measurements in items 1 and 2 at test temperatures (up to 1400 K).

Ultrasound measurements are made by exposing a material to a high-frequency mechanical wave. The waves generated within the sample are then detected and analyzed for frequency, angle and time of transmission. These data can then be related to properties of the materials, or, if the acoustic impedances of the materials in the sample have been measured, the thickness of the various layers in a sample can be calculated.

After discussing the problem with several vendors of ultrasound equipment, it was clear that items 1 and 2 were easily within the capability of current technology but only at temperatures below ~500 K. This restriction was due to the materials used for the transducer of most existing systems. Item 3 would also be relatively straight forward if samples of the pure materials in each layer could be provided to calibrate the measurement instrument. One vendor claimed that capacitively coupling a high temperature transducer could provide test data at temperature. Unfortunately, after much investigation, this technique could not be demonstrated within the time and budget constraints of the program.

Regarding the ability to measure the distribution of the niobium in the ceramic phase, there were again claims these measurements are already within the capability of the technology, but a special transducer of the correct energy, spot size and frequency would need to be developed for the specific application. Preliminary measurements were performed to determine the acoustic impedances for the individual layers, but the hardware development needed was beyond the scope of this program. For these tests the samples were immersed in water and excited by a 200 MHz probe held 1.1 cm from the surface of the material. The wave velocities in the cermet (V_c) calculated by probing different regions of the insulator package are in general agreement.

Some error was expected since no correction was possible for interfacial impedance or plasma sprayed material in the guard-ring. Considering the expected errors, the calculated wave velocities in the cermet appear consistent. Accurate knowledge of this velocity would be vital to the interpretation of any future ultrasonic test data on insulator packages. A summary of the data from these measurements is given in Table 4.3-1.

TABLE 4.3-1

Data Summary for Ultrasonic Analyses
of AL_2O_3 Cermet

<u>Probing Point</u>	<u>t (sec)</u>	<u>d_n (cm)</u>	<u>d_c (cm)</u>	<u>V (cm/sec)</u>	<u>V_c (cm/sec)</u>
Body	3.6×10^{-7}	.163	.066	6.33×10^5	2.93×10^6
Inside guard	2.38×10^{-7}	.102	.066	6.39×10^5	2.46×10^6

V_n = wave velocity in niobium = 4.83×10^5 cm/sec (known)

V_c = wave velocity in cermet (calculated from test data)

V = mean wave velocity = $(d_n + d_c)/t$

d_n = niobium thickness

d_c = cermet thickness

t = wave time-of-flight through sample = $V_n/d_n + V_c/d_c$

To summarize the results of the efforts in this subtask, it was concluded that making the desired measurements for items 1-3 at room temperature and slightly above (up to ~500 K) are well within the range of existing technology. Hardware for the specific needs of sheath insulators will require the development of specific hardware and software for analysis, but this development should be relatively straightforward. Item 4, while possible for current technology, will require substantially more development before it would be useful for this application. Transducers for making measurements at operating temperatures do not presently exist and would require considerable development effort to be made operational with significant further work needed to deal with the problems of shielding from noise and interpretation of data.

4.4 PROCUREMENT AND TESTING OF ALTERNATIVE MATERIALS

The designs presently being developed for sheath insulators are modifications to technologies that were developed prior to 1973 during earlier thermionic programs. Because materials technology has made great strides since that time, specifically in the areas of ultrapure materials processing, ceramic-to-metal joining and production of single crystal materials, a subtask was created to investigate if any of these advances could be readily applied to sheath insulator technology.

When studying the basic problem of material transport in ceramics near 1100 K, it is generally assumed that transport along grain boundaries will dominate lattice transport, especially in Al_2O_3 . Therefore it seems reasonable that if grain boundary area can be reduced or eliminated, material transport could be greatly reduced. Because of great improvement in production of large, single-crystal Al_2O_3 (sapphire) in many geometries, a source of sapphire bonded to niobium was sought. Two sources were located. The first used a reaction bonding method to join the two materials. A layer of glass which reacted slightly with both materials upon melting was used to make the bond. The composition was proprietary to the manufacturer. The result was a strongly bonded flat plate sample of Nb/sapphire/Nb. The sample performed well during resistance testing for one week (Fig. 4.4-1) but had to be removed from the test due to problems with testing flat plate samples in the isothermal ovens. There was evidence of spraying from the glass joining area during testing, but further heating indicated that this was a temporary condition. The Nb/sapphire bonds remained strong despite the loss of material from the bonding layer. The manufacturer claimed to be able to duplicate this for cylindrical geometries, but development costs were beyond the scope of this program.

Another source was found for diffusion bonded Nb/sapphire/Nb layers. This method is strongly preferred since it does not introduce new materials, which could contaminate the sapphire, to the system. Unfortunately, this source was located late in the program at a research facility in West Germany, so samples could not be obtained in time for testing. The technology has, however, been extant for over 5 years and is reported to be very reliable (3).

Fig. 4.4-1 Resistivity of sapphire sample reaction bonded to niobium. Test terminated prior to failure.

Another consideration which led to the investigation of other materials was that, due to their low thermal conductivity, oxide insulators must be very thin (generally $<.5$ mm) to minimize efficiency losses which occur if a substantial temperature gradient exists through the sheath insulator. This limits their resistance and mechanical strength. Recent advances in ultrapure processing have improved the thermal conductivity of nitrides, particularly aluminum nitride (AlN), by as much as a factor of 4 over the accepted values reported in the general literature (4). Therefore, even though AlN has a lower electrical resistivity than most oxides under consideration for thermionic applications, the ability to use a thicker layer with no efficiency penalty may make it attractive for this use. It also has the advantage of having a bond structure that is substantially covalent, which should reduce its tendency toward ionic conductivity and thereby degradation by electrolysis.

While several sources for sintered AlN were identified, only one could deliver high purity samples with a room temperature thermal conductivity of 230 W/m K. This is a factor of 10 better than that reported for alumina. Several samples of this material were received from the manufacturer. The thermal expansion coefficient of AlN is much smaller than that of niobium; it has a much better match with molybdenum, which has also been shown to be a suitable collector material. One sample of the material was received from the manufacturer with molybdenum electrodes brazed to the surface.

Because the samples of AlN were flat plates, they were not life tested because of a lack of a test rig. No cylindrical samples of this material could be obtained within the time constraints of the contract.

5.0 LIFE PREDICTION FOR SHEATH INSULATORS

The degradation of sheath insulator performance is due to the transport of material either out of or into the ceramic layer of the sheath insulator package. Failure can occur because the insulator either 1) ceases to conduct heat; 2) ceases to have a sufficient overall electrical resistance or 3) breaks in such a way as to allow either cesium to escape or coolant to leak in. This life prediction model will focus on cases 1 and 2 only. Transport of material in the insulator package is driven by electrochemical potential gradients within the insulator package. These gradients arise from both chemical gradients (e.g., an oxygen potential gradient) and electrical gradients due to applied potential. Electrical gradients only affect charged species and therefore are important only when a material has an appreciable ionic conductivity. Fluxes due to chemical gradients will be present both with and without the application of an external voltage.

The most likely conceivable causes for failure of the sheath as an electrical insulator are believed to be caused by changes in the microstructure which reduce the material's resistance. These include contamination of the crystal lattices resulting in changes to the bulk resistivity or the formation of a conductive phase(s) along the grain boundaries or insulator surfaces (ends). The latter mechanism seems more likely, since grain boundary diffusivities are probably higher for most substances at the temperature of operation (1100K), and because the grains or grain boundaries themselves could act as sources of material for the formation of such phases. In the case of the cermet approach, the niobium spheres would be distributed throughout the ceramic layer and, therefore, also be a source of material for the formation of such phases. In this case, a change in bulk resistivity also would be a reasonable cause for failure, if niobium is a dopant for the ceramic material.

The most probable cause for failure as a thermal conductor would be formation of a crack at the interfaces between the metal and ceramic, or separation along the grain boundaries. Cracking or separating at the interfaces could be due to the removal of material from the interface by (electro)chemical transport or stresses due to the buildup of material at the

interfaces by similar means. Examples of the latter problem might be the formation of a niobium oxide phase at the interface that could cause stresses sufficient to create a crack due to lattice or expansion mismatches or the piling up of the metal ions from the ceramic phase at the interface causing similar stresses to occur. Grain boundary separation within the ceramic would result if transport along grain boundaries was sufficiently faster than within the grains or if changes in grain dimensions were anisotropic.

The upshot of all of these considerations is the realization that the flux of any species in the system (niobium, oxygen, the metal ion(s) in the ceramic phase(s) or impurities) may be the overriding concern for degradation of insulator performance. The interaction of the individual fluxes may also be the fatal problem, and these problems may vary for insulator designs and materials. Given these considerations it seems most appropriate that a general model for the fluxes of various species be created for a general insulator system. Using this general approach, a number of cases may be defined which represent various materials, assumptions about insulator environment, dominant transport mechanisms and causes for failure. The more likely of these may be further developed. These could then be compared with experiments and further refined based on these observations.

Theory

The general approach to the model involves following the flux of a species, i , from its origin in response to (electro)chemical gradients. The idea is that the species will move across this gradient according to the laws governing solid state transport until an interface is reached. At this interface the species will either 1) continue to follow the gradient with a new diffusivity (or mobility) or 2) be absorbed at the interface by a chemical reaction. For example, an Al^{3+} interstitial in the Al_2O_3 lattice will be influenced by both potential gradients. The interstitial will be driven across the alumina layer by the electric field as well as by the aluminum activity gradient across the Nb- Al_2O_3 interface. The latter driving force is significant only very near the interface, at least until appreciable transport of aluminum has occurred. Once driven to the interface, the Al^{3+} ion will undergo the following reaction

up to the solubility limit of Al in Nb. Niobium is an electronic conductor so there will be an insignificant electric field in this layer and the transport will no longer be driven by that potential. Further motion of this ion will be driven by the aluminum activity gradient across the niobium layer. The rate of this transport will depend on the diffusivity of Al in Nb, which is apparently quite low based upon the findings of Ruhle (3).

To summarize, the species undergoes a chemical reaction of some sort and then responds to its new appropriate driving force with its new diffusivity (or mobility). Therefore, the rate limiting step for transport may be either the chemical reaction or diffusion.

Definition of General System

A schematic of the generalized system to be used for the model is shown in Fig. 5.0-1. This figure indicates six regions indicated by the letters a-f corresponding to the interelectrode gap (cesium vapor), the trilayer and the coolant, respectively. The solid regions b-d also have subregions b', c', d' and e', which correspond to the phases or charged regions along the grain boundaries. No attempt at this time will be made to model the effect of the suspended niobium in phase c on the transport of a particular species across this layer. Where appropriate (i.e., for the cermet), these niobium spheres will be considered as a source of niobium or a sink for other species if phenomena occurring in the bulk of layer c seem significant. Except in the case of Nb ions doping the oxide or reacting with the grain boundary phase, the largest areas of concern will be the b-c and c-d interfaces. The surface area of the niobium spheres can be treated as 'free' surfaces within the system, which may represent increased diffusion rates for certain species. Layers a and f will only be of interest with respect to their roles as sources or sinks for the various species, their roles in establishing the chemical gradients present in the system and their rates of reaction with the various species at the interfaces with the metal layers.

Liquid metal (f)

Cesium vapor (a)

Fig. 5.0-1 Schematic diagram of sheath insulator
for diffusion model.

Given this general picture, the species which will be of interest will be (assuming no penetration/interaction involving Cs, Li, Na or K) Nb, O, M (the metal in the metal oxide) and impurities within the solid layers. The flux of impurities will not be included in the analytical section and will be only generally discussed. The model would need to be updated if impurity fluxes were experimentally determined to be important; in principle this would be straightforward, although reliable data regarding the movement of impurity ions in metals is scarce and very rare for oxides. In the case of intentionally doped oxides, this omission is certainly questionable.

Since most of the layers and interfaces will have very different transport phenomena, the theoretical discussions will deal with each separately before bringing the pieces together. Transport in metal oxide crystals (layer c) which exhibit mixed conduction is discussed first. This is then coupled with the effect of grain boundaries (c') on transport in these systems. The next section covers transport in niobium (b, d, e) and includes a short discussion of grain boundary effects (b', d', and e'). These previous sections are brought together for analysis of the niobium-metal oxide interfaces (b-c and c-d). An analysis of the relevant aspects of the fluid-niobium interfaces (a-b and e-f) follows. The various aspects are then combined for an overall analytical appearance.

5.1 TRANSPORT IN METAL OXIDE CRYSTALS

Mass transport will occur at sufficiently high temperatures in binary metal oxide crystals which are exposed to an oxygen potential gradient or an electric potential gradient. In binary metal oxides, it is unnecessary to state that transport will occur in a metal potential gradient, as the metal and oxygen potential gradients are interrelated, one never existing without the other. For the sake of clarity, transport due to chemical potential gradients will be termed 'chemical diffusion' and that due to electric potential gradients 'ionic conduction'. Transport in oxides occurs via lattice defects which may be charged or uncharged. Charged defects are driven by both chemical and electric potential gradients, while uncharged defects respond only to chemical potential gradients.

Defect Concentrations

The transport of various species in oxide crystals is directly related to the concentration and charge of defects within the crystal lattice. The type and number of defects in a given compound MO is a function of temperature, oxygen pressure, deviations from stoichiometry and concentrations of dopants. Various types of defects, along with their Kroger-Vink notation, are shown in Table 5.1-1.

TABLE 5.1-1 (from (5))

<u>Defect Type</u>	<u>Effective Charge</u>	<u>Kroger-Vink Notation</u>
electron	-1	e'
hole	+1	$h^\cdot$
metal vacancy	0	V_M
metal vacancy	-1	V_M'
metal vacancy	-2	V_M''
oxygen vacancy	0	V_O
oxygen vacancy	+1	$V_O^\cdot$
oxygen vacancy	+2	$V_O^{\cdot\cdot}$
metal interstitial	0	M_i
oxygen interstitial	0	O_i
metal in a normal lattice site	0	M_M
divalent metal M in a lattice site normally occupied by a divalent metal N	0	M_N
divalent metal M in a lattice site normally occupied by a trivalent metal N	-1	M_N'
divalent metal M in a lattice site normally occupied by a monovalent metal N	+1	$M_N^\cdot$
Oxygen in a normal lattice site	0	O_O

Therefore, one must know the value of the above parameters and their relationship to the concentrations of various defects in order to estimate the flux of material within metal oxides. This estimation is accomplished by first writing equations for the creation of various defects. For example, for a stoichiometric compound MO one can write the following reactions

with the following equilibrium constants

$$K_1 = [M_i^{\cdot\cdot}] [V_M''] \quad [5.1-3]$$

$$K_2 = [O_i''] [V_O^{\cdot\cdot}] \quad [5.1-4]$$

and since electroneutrality must be maintained and the compound is stoichiometric, for example, from equation [5.1-1]:

$$[M_i^{\cdot\cdot}] = [V_M''] = k_1^{1/2} \quad [5.1-5]$$

These equilibrium constants are related to the free energy of formation of the defect (ΔG_f) and temperature by the relation

$$K = \exp \left(\frac{-\Delta G_f}{RT} \right) \quad [5.1-6]$$

For most oxides, however, exact stoichiometry exists only over a narrow range of oxygen activity. There is a small deviation from stoichiometry (δ) which can be represented for the above compound as $M_{1-\delta}O$, where δ can be positive or negative depending on whether the crystal is deficient in metal or oxygen, respectively. This non-stoichiometry is due to the necessity of the crystal to be in thermodynamic equilibrium with its surroundings. Most typically the surroundings are thermodynamically defined by specifying its oxygen activity (a_{O_2}), which for small activities (<1 atm) is frequently

equated with the oxygen partial pressure (P_{O_2}). These quantities are equivalent for low activities when the surrounding phase is a gas.

Using oxygen vacancies as an example, the reactions for the formation of defects in a compound $M_{1-\delta}O$ can be written as follows:

Using the corresponding equilibria equations and applying electroneutrality,

$$[e'] = [V_O^\cdot] + 2 [V_O^{\cdot\cdot}] \quad [5.1-10]$$

combining and rearranging yields

$$[e']^3 = k_7 k_8 P_{O_2}^{-1/2} (2k_9 + [e']) \quad [5.1-11]$$

which has two limiting solutions. When $[e'] \gg 2k_9$ (i.e. when singly-charged vacancies dominate

$$[V_O^\cdot] \approx [e'] = (k_7 k_8)^{1/2} P_{O_2}^{-1/4} \quad [5.1-12]$$

or when $2k_9 \gg [e']$ (i.e., doubly-charged vacancies dominate)

$$[V_O^{\cdot\cdot}] = \left[\frac{e'}{2} \right] = \left(\frac{1}{4} k_7 k_8 k_9 \right)^{1/3} P_{O_2}^{-1/6} \quad [5.1-13]$$

This is the case which is considered most likely for the oxides that we are interested in for this study. It is also possible that uncharged vacancies could dominate, which would cause the vacancy concentration to vary linearly with $P_{O_2}^{-1/2}$.

The above equations allow prediction of the dependence of the concentration of defects on oxygen pressure (activity) as long as the predominant defects are known. Often, this dependence is shown on a Kroger-Vink diagram, such as that shown in Figs. 5.1-1 a and b (6). Note that these diagrams assume that fully-charged cation defects dominate in a $M_{1-\delta}O$ compound.

An important feature to notice in these diagrams is that there are plateau regions representing the lowest total concentration of defects in an intermediate oxygen activity range. While this range varies for different metal oxides, it is clear that trends which appear in the higher oxygen activity ranges do not apply at low activity. This clearly indicates the danger of extrapolation of the conductivities of various defects, which are directly proportional to their concentrations, from high activity data to low activities.

Another important consideration is the effect of impurities on defect concentrations. The incorporation of a compound N_2O_3 into the crystal lattice of compound MO (assuming fully charged defects) can be represented by

thereby increasing the concentration of metal vacancies. Similar equations can be written for oxides with metals of higher or lower valence, which also effects the concentration of interstitials or vacancies.

In the above case, the important point is that when the concentration of the impurity N_2O_3 greatly exceeds the intrinsic concentration of defects, metal vacancy concentration will be greatly increased, and therefore, the predominant mass fluxes altered significantly. This is always the case for Al_2O_3 and so is an important consideration for sheath insulator development.

Fig. 5.1-1 a and b Kroger-Vink diagrams for defect concentrations as functions oxygen pressure. a) intrinsic electronic defects dominate b) intrinsic ionic defects dominate

Flux Equations

Transport of matter within oxide crystals is here described as the result of one (or both) of two driving forces, chemical potential (activity) or electric potential. These driving forces can be the result of applied differentials in the potentials, and either of the two can result from one another. These potential gradients can also result from temperature and stress gradients, but for this analysis, these will be ignored.

The two fluxes will be referred to as diffusion and drift respectively.

In the case of diffusion, the flux j_i is described by

$$j_i = \frac{-D_i C_i}{RT} \frac{\delta \mu_i}{\delta x} \quad [5.1-15]$$

This condition is true for all species, i , in the compound. The quantities D_i , C_i , T and $\frac{\delta \mu_i}{\delta x}$ all strongly affect the flux of each species. Equation 5.1-15 can be rewritten (6)

$$j_i = -\tilde{D}_i \frac{\delta C_i}{\delta x} \quad [5.1-16]$$

where the chemical diffusion coefficient, $\tilde{D}_i$, is related to the self diffusion coefficient, D_i , by the relation

$$\tilde{D}_i = (1 + |z_i|) D_i \frac{1}{C_i} \quad [5.1-17]$$

In the case of drift the flux is described by,

$$j_i = \frac{z_i F D_i C_i}{RT} \frac{\delta \phi}{\delta x} \quad [5.1-18]$$

or as more commonly expressed

$$j_i = \frac{\sigma_i}{Z_i F} \frac{\delta \phi}{\delta x} \quad [5.1-19]$$

Often the conductivity of a particular species is expressed as

$$\sigma_i = t_i \sigma \quad [5.1-20]$$

since the total electrical conductivity is easily measured. The transference number, t_i , is simply the fraction of the total current being carried by species i . This still leaves the more difficult task of determining t_i .

Summary of Existing Data

In the above flux equations, D_i (or $\tilde{D}_i$) and C_i cannot be specified; they are properties of the material. They can be determined by various methods, but such data rarely exist and must be either measured or estimated. Some measurements have been made for Al_2O_3 and Y_2O_3 , and these are summarized below.

Al_2O_3

Along with MgO and SiO_2 , Al_2O_3 is the most extensively studied oxide material, with the most thorough work being that of Kroger and associates (7-11). Alumina has a large (~9.9 eV) band gap and a highly ordered structure, having <1 ppm of intrinsic point defects at 1100K. Since the impurity level of Al_2O_3 is always >1 ppm, it follows that the defect structure of Al_2O_3 is dominated by the effects of impurities. Kroger, et. al., have studied the electronic and ionic conductivity of Al_2O_3 doped with various impurities, including Fe, Mg, Co, V, Ti, Y, H, and Si. They have shown that divalent cation impurities such as Fe (7) and Mg (8), act as acceptors, which causes the electronic conductivity of Al_2O_3 to be reduced relative to the ionic conductivity as the oxygen activity is decreased, (Fig. 5.1-2). Tetravalent ions such as Ti (9) and Si (10), which act as donors, have the opposite effect

Fig. 5.1-2 Electronic, ionic and total conductivities of acceptor (Mg) doped alumina.

Fig. 5.1-3 Conductivities of donor (Ti) doped alumina

(Fig. 5.1-3). Experiments with Y, which is isoelectronic with Al, indicate it acts as a donor (11), but this finding has been disputed (12). The observed reduction in ionic conductivity may be due to a suppression in solubility of acceptors as Y is added, followed by segregation of these acceptors to internal or external surfaces.

When comparing the data in Figs. 5.1-2 and 5.1-3 with the generalized Kroger-Vink diagram in Fig. 5.1-1, it is important to note that these data represent only part of the picture. The effect of reduced O_2 pressure is investigated only down to 10^{-3} Pa. This is about 20 orders of magnitude higher than the equilibrium pressure associated with Nb/NbO, which is the maximum equilibrium O_2 activity which will be present in the insulator sheath. It is very likely the ionic contribution to the conductivity, as well as the overall conductivity will begin to rise at sufficiently low P_{O_2} , possibly in the form of oxygen vacancies or aluminum interstitials instead of aluminum vacancies. Therefore, while these data are interesting, their use for prediction of electronic behavior of Al_2O_3 at very low P_{O_2} could be misleading.

Data of Pappis and Kingery (13) and Kitazawa and Coble (14) are shown in Figs. 5.1-4 a and b, respectively. These data show the effect of temperature and oxygen activity on total conductivity to $P_{O_2} < 10^{-10}$ atm. Fig. 5.1-4b illustrates a clear rise in conductivity with decreasing P_{O_2} . While this increase occurs at increasingly low P_{O_2} as temperature decreases, interpolation of the data to 800°C would indicate that the increase would occur near $P_{O_2} = 10^{-22}$ atm with an overall conductivity of $\sim 10^{-11}$ (ohm cm) $^{-1}$. This is near 10^{-12} (ohm cm) $^{-1}$, which has been estimated as a maximum acceptable ionic conductivity for a seven year lifetime. Therefore, if $t_i < 0.1$ (and the extrapolation is at all valid), this requirement can perhaps be met. The interpolation definitely neglects the increasing importance of grain-boundary transport with decreasing temperature. This phenomena will be discussed in more detail on the next section.

Fig. 5.1-4 a Electrical conductivity of single crystal Al₂O₃ as a function of oxygen partial pressure.

Fig. 5.1-4 b Conductivity isotherms for single crystal Al_2O_3 from K. Kitazawa and R. L. Coble (14).

Self diffusion coefficients for Al and O in Al_2O_3 have been measured by various investigators (15-18) although there is some disagreement. These data are summarized in Fig. 5.1-5. The larger value for Al diffusion, coupled with the estimation that Al interstitials will be the most prevalent defect indicates that transport of Al may play a dominant role in degradation of Al_2O_3 .

Diffusion studies of O (19) and Y (20,21) in Y_2O_3 indicate that oxygen diffusion coefficients are 2 to 4 orders of magnitude greater than those of yttrium, although the oxygen data were obtained in an oxygen potential gradient. A summary of these results is in Figure 5.1-6. The discrepancy in the data for yttrium is attributed to a higher porosity in the samples which resulted in the higher values. This indicates a much higher surface diffusion coefficient and a lower activation energy for this process.

The most widely cited data for Y_2O_3 conductivity as a function of P_{O_2} is that of Tallan and Vest (22). These results indicate that the conduction is mixed at low P_{O_2} and temperatures of $< 1000^\circ\text{C}$, but some reviewers question these conclusions (23). Tare and Schmalzreid (24) found Y_2O_3 to be a pure ionic conductor at 825°C between 10^{-4} and 10^{-20} atm O_2 . These discrepancies are attributed to the possibility that the Tallan and Vest data represent extrinsic conduction and/or problems with the blocking electrode (21). Recent studies by Norby and Kofstad (25) indicate the effects of O_2 pressure on conductivity in Y_2O_3 but do not extend to low oxygen pressures. In any event, the conductivity of Y_2O_3 in the region of interest is probably substantially ($t_i > 0.1$) ionic, and total conductivity is on the order of $10^{-6} (\text{ohm cm})^{-1}$, making ionic transport a definite concern.

5.2 EFFECTS OF GRAIN BOUNDARIES

Most materials currently under consideration for sheath insulators are polycrystalline materials. This means that to estimate transport of material through the insulating layers properly one must also estimate the rate of

OXIDES OF GROUP IB-VB ELEMENTS

Fig. 5.1-5 Arrhenius plot of results of aluminum and oxygen self-diffusion in Al₂O₃.

Fig. 5.1-6 Self-diffusion coefficients in Y₂O₃

transport through the grain boundaries. This area is not well understood but can be approximated by considering a series of limiting cases. It is generally true that impurities in oxide ceramics tend to segregate along the grain boundaries, sometimes by factors of tens or even hundreds of times greater than the bulk concentration. This means that materials with impurities of >100 ppm could easily have grain boundary impurities of >1%. Often times this is above the solubility limit for a particular impurity or group of impurities, which would result in the precipitation of a second phase along the grain boundaries. Whether or not a second phase does exist, it is almost certain that the defect concentrations and diffusion coefficients along grain boundaries will be different than those in the bulk crystal. These facts can cause the grain boundaries to have quite different effects on transport due to diffusion and that due to drift.

In the case of diffusion, it is usually true that the diffusion coefficient of a particular species is significantly larger within a grain boundary than within the crystal lattice at temperatures less than one half of the melting point. This stems from the (generally) looser packing within these interfaces. This may not be true where grains are surrounded by a second phase, in which case diffusion will be controlled by the mobility in the new phase which may be totally unrelated to the original diffusivity.

The result of this enhanced diffusion is that average rates of migration within these polycrystalline material is faster than those predicted by models for single crystals. One approach to predicting the diffusion rates in polycrystalline materials is the sphere model, as expanded by Oishi and Ichimura (25). The following paragraphs are a summary of the results of this analysis. The reader is referred to the paper for details of the derivations. This model assumes the material to consist of equal sized polyhedrons, which can be approximated as equal-sized spheres (Fig. 5.2-1). The sphere radius is set equal to one half of the average grain size. The basic equation governing the concentration of a species is:

$$\frac{\delta C_i}{\delta t} = D \frac{\delta^2 C_i}{\delta x^2} + \frac{2D}{\delta} \frac{\delta C_i}{\delta y} \quad y = \delta/2 \quad [5.2-1]$$

Fig. 5.2-1 A schematic diagram of the grain-boundary enhanced diffusion model for spherical grains.

with the boundary conditions

$$C_i = C_{0i}, x = 0, t \geq 0$$

$$C_i = \phi_{xi}, x > 0, y = 0 \quad t > 0 \quad [5.2-2]$$

$$C_i = C_{1i}, x > 0, 0 < y < r, t = 0$$

$$C_i = f(y) \quad 0 < y < r, t > 0$$

where r = sphere radius

C_0 = initial concentration at the insulator interface

C_1 = concentration within crystals at $t = 0$

ϕ_x = average concentration within the grain boundary at x

D' = grain boundary diffusion coefficient

D = lattice diffusion coefficient

δ = grain boundary width

The model also assumes $D' \gg D$. This allows one to determine the concentration distribution within the sphere at constant ϕ_x , with only small error. Exploitation of this approximation for the case of $x \gg r$ allows one to arrive at

$$\frac{\bar{C} - C_1}{C_0 - C_1} = \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-a) \right] \quad [5.2-3]$$

$$\times \exp \left[- \left[\frac{4D}{r\delta D'} \sum_{n=1}^{\infty} \exp(-a) \right]^{1/2} x \right]$$

where $\bar{C}$ = average concentration at distance x from the interface.

$$a = \frac{Dn^2\pi^2t}{r^2}$$

Plotting $\ln \left[\frac{\bar{C} - C_1}{C_0 - C_1} \right]$ allows the determination of the value of D and $\delta D'$.

$\bar{C}$ can be determined by sectioning or electron microprobe analyses. From the form of the equation it is obvious that at steady state ($t = \infty$) $\bar{C} = C_0$.

As mentioned previously, one of the possible mechanisms for failure would be separation at the metal-ceramic interface. For mass transport in this area, direct diffusion from or into the the metal layer cannot be neglected so in this region ($x \leq 2r$) equation [5.2-3] becomes

$$\frac{C - C_1}{C_0 - C_1} = \operatorname{erfc} \frac{x}{2\sqrt{Dt}} + \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-a) \right] \\ \times \exp \left(- \left[\frac{4D}{r\delta D'} \sum_{n=1}^{\infty} \exp(-a) \right]^{1/2} x \right)$$

Diffusion in grain boundaries can also contribute to failure due to grain boundary separation. The mechanism for this type of failure is less well understood, but a plausible cause could be anisotropic transport of materials within the grains. This transport could cause the crystals to grow in one direction while shrinking in another. Also, as the crystal lattice becomes preferential depleted of either anions or cations, the packing of atoms in the resulting structure may become less dense. Either case could cause stresses which result in cracking at the grain boundaries. Rapid diffusion of a viscous phase along the grain boundaries could also lead to separation by creep, but this seems less likely. Due to the uncertainty and complicated,

material-specific nature of these mechanisms, this work will not attempt to model these situations. Further work to understand this problem would be useful, however, especially since the situation will almost certainly be exaggerated by neutron fluence.

With respect to drift, grain boundaries could play a very different role. It is very likely that the conductivities of ions and electrons in the grain boundary will differ from those in the grain, especially if the grain boundary consists of a second phase. In any case, the grain boundary could easily impede the drift of charged species as has been shown in solid electrolytes (26). The situation is analogous to that of a so-called 'blocking' electrode. A blocking electrode either completely or more often nearly-completely stops the drift of charged species, due to the lack of conductivity of that species within that electrode. For example, non-porous gold makes a good blocking electrode for oxygen, while Y_2O_3 stabilized ThO_2 is a good blocking electrode for electrons, because it is a pure ionic conductor at most oxygen activities and temperatures (27).

As an example, the case of an oxygen interstitial moving through a lattice that is essentially a pure ionic conductor approaching a grain boundary that is essentially a pure electronic conductor is illustrated in Fig. 5.2-2. This might be the case when a second phase exists at the grain boundaries. The oxygen vacancies are not mobile in the grain boundary and accumulate at the interface. The initial potential gradients become increasingly steep as oxygen vacancies are blocked at the interface causing the oxygen activity to decrease locally to compensate for the applied potential. Eventually, leakage currents and diffusion across the interfaces due to the steep activity gradients control the flux of oxygen. The opposite will occur at the other interface since no source of oxygen vacancies exists. The drift of ionic species in insulators is usually quite slow. It might be expected, therefore, that the diffusion of these species (especially in the grain boundaries) may be fast enough to even out the chemical potential gradients created by the accumulation of the drifting species. If this is the

Potential and concentration distribution changes in second phase material with electronic conductivity. (a) Soon after current switch-on. Full arrows indicate oxygen flux, the dashed arrow electronic flux. (b) Steep concentration gradients have been formed, and double layer voltages compensate the applied voltage. (c) Diffusion profiles develop starting from the boundaries I and II.

Fig. 5.2-2 General approach of analytical model to transport at phase boundaries.

case, the activity gradients will not become steep enough to be a problem; however, it remains a problem at the metal/ceramic interface, which will be discussed below.

To determine analytically if this blocking effect is a concern for specific insulators, it would be necessary to know the transport numbers, mobility and diffusivity of the species of interest for the lattice and grain boundary phases. Regrettably, this calculation seems totally unrealistic, since these values are not known over a wide range of conditions for even single crystals. Therefore, it would seem most reasonable to approach this problem experimentally by the use of AC impedance spectroscopy. This technique allows a qualitative understanding of the polarization resistance at interfaces such as grain boundaries to the transport of ionic charge carriers. Even this experimental effort represents a considerable effort. If grain boundary separation proves to be a significant failure mechanism, some method of understanding the transport phenomena in these regions will be necessary to logically guide further development efforts.

5.3 IONIC TRANSPORT IN NB AND NB/1%ZR

While there is still much to learn, transport of ions through metals is much better understood than through ionic materials. For niobium, the diffusion coefficients for several elements have been measured, especially between 1100 and 2000 K. The known data for ions anticipated to be of importance in the cladding layers on sheath insulators with liquid metal coolants are summarized in Table 5.3-1. As can be seen from these data, the diffusion coefficients of oxygen and nitrogen are >4 orders of magnitude higher than other ions present in this system at 1100 K. This fact has not escaped the attention of researchers and has led to investigation of these diffusion coefficients in niobium alloys (28, 29), the energies of formation of Nb-O solid solutions (30, 31) and the effect of small amounts of oxygen on the mechanical properties of niobium (32). The data from these latter studies have provided a method for measuring the concentration of O in Nb by

microhardness measurements, since the addition of O to Nb causes considerable embrittlement in the metal. The enhanced diffusion of O in Nb coupled with the emphasis given to oxide ceramics also justifies the emphasis to O transport that is given below.

TABLE 5.3-1

Transport Data for Niobium
Diffusion Coefficient (D) evaluated by $D = A \exp (-E_d/RT)$

<u>Diffusing Species</u>	<u>Temperature Range (K)</u>	<u>A (cm²/sec)</u>	<u>^oE_d (kJ/mole)</u>	<u>Example D (cm²/sec)</u>
Nb	1873 - 2273	18.18	473.1	$D_{1873} = 1.18 \times 10^{-12}$ (5)
Y	1473 - 1873	1.5×10^{-3}	232.8	$D_{1473} = 8.4 \times 10^{-12}$ (5)
Na	1173 - 1373	1.611×10^{-9}	77.9	$D_{1373} = 1.76 \times 10^{-12}$ (5)
N	543 - 2073	2.6×10^{-2}	152.3	$D_{1100} = 1.53 \times 10^{-9}$, $D_{1333} = 2.81 \times 10^{-8}$ (33)
O	413 - 1273	5.3×10^{-3}	109.5	$D_{1100} = 3.35 \times 10^{-8}$ (33)

In principle, the equations governing the transport of ions through metals are the same as those for metal oxides. A major difference for the case at hand, however, is the relative unimportance of the driving force of the electric potential gradient in the niobium and Nb/1%Zr layers, due to their much lower resistivity and essentially pure electronic conductivity. This fact allows the assumption that this driving force is negligible compared to the chemical driving force.

Making this simplifying assumption, the flux of species i can be described by

$$J_i = -D_i \frac{\delta C_i}{\delta x} \quad [5.3-1]$$

and applying the continuity equation yields:

$$\frac{\delta C_i}{\delta t} = \frac{-D_i \delta^2 C_i}{\delta x^2} \quad [5.3.-2]$$

i.e., Fick's Law.

Since the diffusion coefficients of the ions of interest are known, all that is left is to determine the boundary conditions for the metal layers. For the inner Nb layer (b):

$$@ \ x_a - b \text{ (the Nb - Cs interface)} \quad \mu_{ia} = \mu_{ib} \quad [5.3 - 3a]$$

$$@ \ x_b - c \quad \mu_{ib} = \mu_{ic} \quad [5.3 - 3b]$$

$$@ \ t = 0 \quad \frac{\delta C}{\delta x} = 0, \ C_i = C_{i0} \text{ for } x_{a-b} < x < x_{b-c} \quad [5.3 - 3c]$$

and the outer Nb layer (d):

$$@ \ x_{c-d} \quad \mu_{ic} = \mu_{id} \quad [5.3 - 4a]$$

$$@ \ x_{d-e} \quad C_{ie} = C_{id} \quad [5.3 - 4b]$$

$$@ \ t = 0 \quad C_i = C_{i0}, \ \frac{\delta C}{\delta x} = 0 \text{ for } x_{c-d} < x < x_{d-e} \quad [5.3 - 4c]$$

and the Nb/1%Zr layer (e):

$$@ \ x_{e-f} \quad \mu_{ie} = \mu_{if} \quad [5.3 - 5a]$$

$$@ \ x_{d-e} \quad C_{ie} = C_{id} \quad [5.3 - 5b]$$

$$@ \ t = 0 \quad C_{ie} = C_{ie}^0 \text{ for } x_{d-e} < x < x_{e-f} \quad [5.3 - 5c]$$

For oxygen and nitrogen it is also reasonable to assume that

$$C_{ib}^o = C_{id}^o = C_{ie}^o \quad \text{and} \quad \mu_{ic}^o = \mu_{ib}^o = \mu_{id}^o = \mu_{ie}^o$$

The relationship of the chemical activities for the various components in the adjacent phases to the concentration of these components and the rates of reactions across interfaces will be discussed in Section 5.4.

The Effect of Grain Boundaries

No data regarding the transport of oxygen along grain boundaries in niobium was found and for the purpose of this analysis will be ignored. If grain boundary transport is found to be significant, the equations developed for metal oxides in Section 5.2 should also apply here if the grain boundary diffusivity is much larger than lattice transport.

5.4 INTERFACIAL TRANSPORT AND EQUILIBRIA BETWEEN SOLID-SOLID INTERFACES

Niobium/Metal Oxide Interfaces

Because processing of the insulator packages is finished by hot isostatic pressing (HIP) at high temperature (usually >1600°C), it is a reasonable assumption that the activities of relatively fast-diffusing species will be in equilibrium across the niobium/metal oxide interfaces at the beginning of the tests. This will mean that the initial transport in these phases will be due to the application of the electric field, with further transport resulting from the chemical gradients caused by the migration and the diffusion of species to and from the fluid phases.

While the activities of the species may be equal, the transport equations within each layer are in terms of concentrations. It is necessary to relate

these two quantities for adjacent layers. It is assumed that there are no phase changes within any of the layers, and the accommodation of a particular species from an adjacent layer into the new layer occurs quickly with respect to diffusion (i.e. there is always local equilibrium at these interfaces).

The data needed to relate these two quantities between the metal and metal oxide layers are derived from the thermodynamic data for the dissolution of oxygen in niobium and the defect equations for Al_2O_3 . The data for the defect concentrations in Al_2O_3 , however, do not extend below oxygen activities of $\sim 10^{-10}$ atm O_2 . The relationship between the concentration of O in Nb (x_0 , in atom %) and the equilibrium oxygen activity (a_{O_2} , in atm) is given by (31):

$$a_{\text{O}_2} = x_0^2 \exp \left[2.405 \times 10^{-1} \{-3.8445 \times 10^5/T + 55.4\} \right] \quad [5.4-1]$$

Nb/Nb-1%Zr Interface

Data for dilute niobium alloys suggest that the activity of oxygen in these alloys is very close to that of pure niobium. It is therefore assumed that the concentrations of oxygen as well as its activity will be equal at equilibrium. Since these layers are joined by a nickel layer, the diffusion rates of Ni as well as Zr in Nb and in the alloy are formally at concern here, but both are anticipated to be low enough to prevent significant penetration through the outer Nb layer to the ceramic, where they could affect the life time by doping or grain boundary penetration. The nickel layer is more of a concern as a surface contaminant on the ends of the oxide layer, which could cause failure due to surface conduction.

Transport in Interfacial Regions

Relation of the chemical activities in equations 5.3-3a, 3b, 4a and 5a to concentrations requires knowledge of the thermodynamics of solutions of the element of interest in all layers that the model covers and the kinetics of

any reactions that may limit the rate of exchange of a species between the phases. For convenience, the liquid metal is assumed to have a concentration of <10 ppm O, which is considerably below the saturation level for lithium at 1100 K. It is also assumed that the volume of the liquid metal is sufficient to prevent a significant increase (or decrease) in the concentration of O with time and that the diffusivity of O in the melt is sufficiently greater than that in the metal to prevent the formation of a significant gradient in the melt. This means that the O activity at the Nb-1%Zr/Li interface is $\ll 10^{-36}$ atm O₂. This defines the equilibrium O concentration of the metal at this interface as $\ll 0.01$ a/o. Due to a lack of accurate thermodynamic data regarding the activity of oxygen in lithium at these very low levels, a Raoult's Law linear approximation yields 10^{-40} atm O₂. This represents a serious oxygen potential gradient across the metal layers. A non-zero value must be assumed due to the logarithmic relation between activity and applied potential that will be needed in the analysis below.

The relationship of oxygen concentration and activity in the cesium vapor is poorly characterized, although it is a safe assumption that the O₂ activity is $\ll 10^{-20}$ atm O₂. The problem is further complicated by the very low pressure (<2 mTorr) of the vapor, which may cause the reaction rates (for oxygen leaving the gas to enter the niobium) to be quite low. The overall reaction can be represented by:

Based on experimental observations at RAI, it is probably reasonable to assume that in reaction [5.4-2] $k_1 > k_2$ (34), perhaps by a factor of 10 or more. This assumption is based upon observation of an electrolytic cell being used to transport oxygen into and out of the converter. Oxygen was easily transported into the cell, but removal of oxygen was extremely difficult. This difficulty indicates the affinity of the cesium phase for oxygen. This coupled with the low oxygen activity of the cesium allows the assumption that the flux of oxygen from the vapor to the niobium can be neglected.

5.5 OVERALL MODEL

Given the considerations presented for each layer, it is now possible to combine these into a general set of equations for the entire insulator package. A review of the controlling equations and the relevant species for each layer is given first, followed by a discussion of the likely situations which may lead to insulator failure.

Fig. 5.5-1 shows a schematic of the insulator package with the controlling transport equations and boundary conditions for each layer. The equation for the concentration of a species, i , and its flux, j_i , are given, both in terms of concentrations. It is necessary to determine the transient concentration profiles in order to make reasonable estimates of the fluxes of various species or progression of reduced zones that would accompany electrolysis in the ceramic phase. To solve for the concentration profiles, it will be necessary to solve the equations for the individual layers, while matching the fluxes at each interface as part of the boundary conditions. Due to funding constraints, this solution was beyond the scope of this program. While an overall analytical solution may be possible, a numerical analysis would probably be the most efficient approach to solving the equation system.

Because an overall solution was too ambitious for this program, a greatly simplified analysis is presented below. Using alumina as an example, the effect of the metal layers is ignored, and the steady-state fluxes of oxygen and aluminum are estimated for an insulator at 1100 K, with 15 volts applied.

Fig. 5.5-1 Insulator package showing flux equations and boundary conditions in each phase.

The calculations are based on the assumption of a linear activity gradient throughout the insulator and fixed activities at the solid/insulator interfaces.

Clearly, the insulator will have failed long before this situation arises, but this estimate gives a reasonable upper limit to the values of the flux from the material. The assumption to neglect the effects of the niobium layers is probably valid for oxygen (and nitrogen in the case of nitride insulators) because the diffusion coefficients for these elements are so relatively large that no significant potential gradient across the niobium is anticipated. The resultant errors for metal ions will have to await further enhancements of the model.

The effects of the applied potential, which is expressed in volts, and the chemical driving forces, which are expressed as ratios of activities, are made additive through the relation (35):

$$E = I_e R_e + RT/nF \ln(a_{b-c}/a_{c-d}) \quad [5.5-1]$$

where E = applied potential

I_e = current fraction due to electronic conduction

R_e = resistance to electronic conduction

a_n = activity of the dominant ionic defect at boundary n

and the other symbols have their usual meanings. Rewriting in terms of t_i , the fraction of the voltage which causes ionic conduction of species i , and rearranging, one obtains:

$$\exp[nFt_i E/RT] = a_{b-c}/a_{c-d} \quad [5.5-2]$$

This gives a ratio of activities which can be converted to concentrations using the mass action equations governing the formation of species i . This conversion is unnecessary for the present analysis, but will prove useful when solving the equations of Fig. 5.5-1 for the transient concentration profiles. Unfortunately, t_i is unknown for the materials of interest in the oxygen activity ranges of interest and so must be assumed. In the case of binary systems, such as alumina and yttria, one is aided by the fact that specifying the activity of one component, such as oxygen, automatically fixes the activity of the metal. The effect of the chemical activity gradient can either enhance or reduce the effect of the applied potential depending upon the orientation of the two potential gradients.

Results of this analysis for donor-doped Al_2O_3 are given in Table 5.5-1. Details of the calculations for this and subsequent analyses are given in the Appendix. As can be seen, the resultant fluxes are absurdly small, indicating that the transport of native ions in alumina through the crystal lattice will probably not be the mechanism for insulator failure at 1100 K for donor-doped material. The low fluxes are a result of the low diffusion coefficient of the most mobile species (V_{Al}''') combined with the low concentration of defects. The diffusion coefficient used represents the highest value found in the literature (18), so it is unlikely to be the source of an underestimate of the flux. The concentration, however, has been extrapolated from high temperature conductivity data and adjusted for low oxygen activity using a speculated mass action relationship, which resulted in a 1000-fold reduction in concentration of defects. However, even if this correction were in the wrong direction, the predicted time to remove 1% of the aluminum ions would be $>10^4$ years. For this material, surface or grain-boundary diffusion of either native ions or impurities, enhanced transport due to neutron fluence, or cracking due to swelling from neutron damage are more likely avenues of failure. With the exception of the latter mechanism, the theoretical framework for developing models for these failure routes is not well developed. Data needed for grain boundary diffusion and the interaction of neutron-generated defects with electric potential gradients also are lacking.

TABLE 5.5-1

Atomic fluxes in Al_2O_3 (500 ppm Ti) exposed to Li at 15 VDC.
The negative values refer to reversed polarity of the field and
hence diffusion in the opposite direction.

<u>t_i</u>	<u>j_i (atoms/cm² sec)</u>
-1	-210
-0.5	-97
-0.1	-62
0	16.5
0.1	39.3
0.5	130.3
1	244

A similar analysis for yttria is presented in Table 5.5-2. The data available for yttria did not allow for a thorough cross checking of diffusion coefficients and concentrations of defects as was possible for alumina. The data used were those of Norby and Kofstad (19). The defect structure of yttria has been shown to depend strongly on the presence of water vapor and other impurities. The effects of grain boundary diffusion at these temperatures may not be negligible. The data used were not sufficient to consider the effects of all of these parameters on the conductivities and diffusion coefficients used. No correction for the low oxygen pressure in the sheath insulator was possible i.e., the transport parameters used for the calculations were data obtained at $P_{\text{O}_2} = 10^{-10}$ Pa.

TABLE 5.5-2

Oxygen fluxes in Y_2O_3 exposed to Li at 15 V DC. Diffusivities used in calculations are experimental values at $P_{O_2} = 10^{-10}$ Pa.

<u>t_i</u>	<u>j_i (atoms/cm² sec)</u>
-1	-2.3×10^{13}
-0.5	-1.1×10^{13}
-0.1	-6.8×10^{12}
0	1.8×10^{12}
0.1	4.3×10^{12}
0.5	1.4×10^{13}
1	2.7×10^{13}

The data for yttria are remarkably different from those for alumina. Times to achieve a 1% loss of the most mobile species (in this case, oxygen) range from about 61 days to 98 hrs. These estimates are lower limits for the expected loss of oxygen, and besides the errors cited above, there is no evidence that failure occurs at (or even near) 1% loss of oxygen. The data do indicate, however, that electrolysis could be, and probably is, a factor in the failure of yttria sheath insulators. It does not mean that yttria cannot be a useful insulator material, however. The lower oxygen activity in the reactor environment could serve to lower the concentration of defects in yttria. It may also be that the most mobile defect, oxygen, is not the dominant defect under the conditions of interest. Of course, these data will also depend on the type and, to a lesser extent, concentration of dopants and impurities in the yttria. Unfortunately, without a detailed study of these effects coupled with a development program to control the purity during manufacture, the likelihood of developing the correct configuration of yttria is severely limited.

6.0 CONCLUSIONS

1. The four Al_2O_3 - Nb cermet samples all failed rapidly when subjected to electric fields at elevated temperature. Further tests were terminated when the manufacturer discover conductive surface layers on these cermets.
2. A second phase (yttria alumina garnet) was detected on the grain boundaries of these samples. This phase may be related to the rapid failure of the insulating properties of these materials.
3. Two samples showed a very low activation energy for conduction (8.5 kJ/mole) while that derived for the other two was an order of magnitude greater. This indicates that different processes were probably controlling conduction in each of the two pairs of samples, all of which were nominally identical.
4. The use of ultrasonic techniques for the evaluation of insulator packages has good potential, but considerable development would be necessary, especially for in-situ testing at high temperature.
5. The reaction bonded sapphire sample showed good resistance behavior over its limited test period. Its resistance continued to increase over the same time period in which all the cermets had failed.
6. Evaluation of the ionic fluxes through the insulator package due to chemical and electrical potential gradients can be used as a basis for a model to predict insulator lifetime.
7. Rigorous solution of the full model requires values for many physical parameters that are unknown, but a simplified variation of the model can be solved approximately for the ionic fluxes.

8. Solution of the simplified model indicates that alumina should not fail by the depletion of aluminum for thousand of years. Calculations for yttria show a much more rapid depletion of oxygen indicating electrolysis as a possible failure mode for that material.

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APPENDIX A

TTP FLUX CALCULATIONS

Flux due to chemical diffusion:

$$j_i = -D_i C_i \frac{\delta \ln a_i}{\delta x} = \frac{-D_i C_i \ln(a_1/a_2)}{\Delta x} = \frac{-D_i C_i \ln(10^{-25}/10^{-40})}{.0254 \text{ cm}}$$

$$j_i = D_i C_i \quad 1.36 \times 10^3 \text{ atoms/cm}^2 \text{ sec} \quad [\text{A-1}]$$

Total molecules of $\text{Al}_2\text{O}_3/\text{cm}^3 = 2.3 \times 10^{22}/\text{cm}^3$

$$6.9 \times 10^{22} \text{ O atoms/cm}^3$$

$$4.6 \times 10^{22} \text{ Al atoms/cm}^3$$

How many mobile defects exist in 500 ppm Ti doped Al_2O_3 ?

From Kroger @ 1600°C and 500 ppm Ti $\sigma_i \approx 2 \times 10^{-9} \text{ (ohm cm)}^{-1}$

$$\sigma_i = (C_i D_i Z_i^2 e^2) / kT = 9.93 \times 10^{-19} C_i D_i Z_i^2$$

Assuming the dominant mobile defect is V_{Al}''' $Z_i = 3$

$$D_i \approx 1.44 \times 10^{-8} \text{ cm}^2/\text{sec} \quad (\text{from Kroger data})$$

The ionic conductivity and diffusivity combine to give

$$C_i = [V_{\text{Al}}'''] \approx 1.56 \times 10^{16} \text{ cm}^{-3}$$

This concentration is based upon data at $P_{\text{O}_2} = 10^{-9} \text{ atm}$

For constant Ti doping : $[V_{Al}'''] \propto P_{O_2}^{3/16}$

Based upon the data for $P_{O_2} = 10^{-9}$ atm

$$[V_{Al}'''] = 7.6 \times 10^{17} P_{O_2}^{3/16}$$

$$\text{At } P_{O_2} = 10^{-26} \text{ atm} \quad [V_{Al}'''] \approx 1.56 \times 10^{13} \text{ cm}^{-3}$$

Flux due to electric field:

$$j_i = D_i C_i \frac{\delta \ln a_i}{\delta x} \quad \frac{\delta \phi}{\delta x} = \frac{RT}{ZF} \frac{\delta \ln a_i}{\delta x}$$

$$\frac{\delta \ln a_i}{\delta x} = \frac{ZF}{RT} \frac{t_i \Delta \phi}{\Delta x} = \frac{t_i}{.0254 \text{ cm}} \frac{3 \times 96480 \text{ C/mole}}{8.316 \text{ VC/mole K}} \frac{15 \text{ V}}{1100 \text{ K}}$$

$$\frac{\delta \ln a_i}{\delta x} = 1.87 \times 10^4 t_i \text{ cm}^{-1}$$

$$j_i = 1.87 \times 10^4 t_i \text{ cm}^{-1} D_i C_i \quad [A-2]$$

The total flux will be the sum of the fluxes from the two driving forces.
Summing equations A-1 and A-2:

$$j_i (\text{total}) = D_i C_i (1.36 \times 10^3 \pm t_i 1.87 \times 10^4) \quad [A-3]$$

From Kroger: The mobility of V_{Al}''' is given by

$$\mu = 5.2 \times 10^3 \exp (-3.78 \text{ e/kT}) = 2.46 \times 10^{-14} \text{ cm}^2/\text{V sec at 1100 K}$$

$$\mu = \frac{D_i e Z_i}{kT}$$

$$D_i = \frac{\mu kT}{eZ_i} = \frac{2.46 \times 10^{-14} \text{ cm}^2/\text{V sec} \cdot 1100 \text{ K} \cdot 1.38 \times 10^{-23} \text{ J/K}}{1.6 \times 10^{-19} \text{ JV} \cdot 3} = 7.8 \times 10^{-16} \text{ cm}^2/\text{sec}$$

This diffusivity and the estimated defect concentration ($1.56 \times 10^{13} \text{ cm}^{-3}$) were inserted into equation A-3 to calculate the total fluxes listed in Table 5.5-1.

Time to remove 1% of the aluminum?

$$\text{Al atoms to remove} = \frac{4.6 \times 10^{22}}{\text{cm}^3} \cdot 0.0254 \text{ cm} \cdot 0.01 = 1.17 \times 10^{19} \text{ cm}^{-2}$$

$$\text{At the largest flux: } t = \frac{1.17 \times 10^{19} \text{ cm}^{-2}}{244 \text{ cm}^{-2} \text{ sec}^{-1}} = 4.79 \times 10^{16} \text{ sec} \approx 1.5 \times 10^9 \text{ yrs}$$

For Y_2O_3 :

$$\begin{aligned} \text{Total molecules } \text{Y}_2\text{O}_3 &= 1.25 \times 10^{22} \text{ cm}^{-3} \\ &= 3.75 \times 10^{22} \text{ O atoms/cm}^3 \end{aligned}$$

From Norby and Kofstad:

$$\sigma_{\text{ion}} = 1.1 \times 10^{-6} \text{ (ohm cm)}^{-1} \quad \text{at } 1100^\circ\text{C}$$

$$\sigma_i = (C_i D_i Z_i^2 e^2)/kT \quad \therefore D_i C_i = 2 \times 10^{11} \text{ (cm sec)}^{-1} \text{ at } 1100^\circ\text{C}$$

$$D_i \approx 3 \times 10^{-9} \text{ cm}^2/\text{sec} \quad \text{at } 1100^\circ\text{C} \quad \text{from Fig. 5.1-6}$$

$$D_i \approx 2 \times 10^{-11} \text{ cm}^2/\text{sec} \quad \text{at } 1100 \text{ K}$$

$$C_i = 6.7 \times 10^{19} \text{ cm}^{-3} \quad \text{at } 1100^\circ\text{C}$$

Using this concentration as an approximation at 1100 K:

$$D_i C_i = 1.33 \times 10^9 \text{ (cm sec)}^{-1}$$

This gives a total flux of:

$$j_i = 1.33 \times 10^9 \text{ (} 1.36 \times 10^3 \pm t_i 1.87 \times 10^4 \text{)}$$

The fluxes calculated by this equation are listed in Table 5.5-2.

Estimating extreme lifetimes:

$$\text{for } t_i = 0, 1\% \text{ depletion } t = \frac{3.74 \times 10^{22} \cdot 0.01 \cdot 0.0254}{1.8 \times 10^{12}} = 5.28 \times 10^6 \text{ sec} \approx 61 \text{ days}$$

$$\text{for } t_i = 1, 0.1\% \text{ depletion } t = \frac{3.74 \times 10^{22} \cdot 0.001 \cdot 0.0254}{2.7 \times 10^{13}} = 3.5 \times 10^4 \text{ sec} \approx 9.8 \text{ hrs}$$