N71-28035

NASA TECHNICAL MEMORANDUM

NASA TM X-2303

NASA TM X-2303

3000-HOUR ELECTRICAL TEST OF AN ALUMINA TRILAYER AT 1325 K

by John T. Mayer

Lewis Research Center
Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JUNE 1971

1. Report No. NASA TM X-2303	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle 3000-HOUR ELECTRICAL TEST OF AN ALUMINA TRILAYER AT 1325 K	5. Report Date June 1971 6. Performing Organization Code
7. Author(s) John T. Mayer	8. Performing Organization Report No. E-6139
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135	10. Work Unit No. 120-27 11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546	13. Type of Report and Period Covered Technical Memorandum 14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

A thermionic sheath insulator specimen, in the form of a bonded niobium/alumina/niobium cylindrical sandwich, was tested in vacuo with a continuous dc voltage applied, in order to examine possible electrolysis effects. The trilayer resistance remained relatively constant for the first 1000 hours. It then increased (over a period of about 500 hr) by a factor of 5 and remained at this value to the end of the test. Post-test examination revealed no major changes in the gross physical characteristics of the sample. However, some evidence of damage was seen in the photomicrographs.

17. Key Words (Suggested by Author(s)) Aluminum oxide Electrolysis Thermionics Ceramic insulator	18. Distribution Statement Unclassified - unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 15	22. Price* $3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

3000-HOUR ELECTRICAL TEST OF AN ALUMINA TRILAYER AT 1325 K

by John T. Mayer

Lewis Research Center

SUMMARY

A thermionic sheath insulator specimen, in the form of a bonded niobium/alumina/niobium cylindrical sandwich, was tested for 3000 hours with a continuous dc voltage applied, in order to examine possible electrolysis effects. The test conditions were as follows: a temperature of 1300 to 1375 K, a pressure of about 1.3×10^{-4} N/m^2 (10^{-6} torr measured), and dc current averaging 3 milliamperes.

After a slight drop at the beginning of the test, the trilayer resistance remained relatively constant for the first 1000 hours. It then increased (over a period of about 500 hr) by a factor of 5 and remained at this value to the end of the test.

Post-test examination revealed no major changes in the gross physical characteristics of the sample. However, some evidence of grain boundary weakening and niobium-alumina interaction was seen in the photomicrographs.

INTRODUCTION

In a thermionic space power system, the individual collectors in each diode must be electrically insulated from the coolant sheath (see fig. 1). Some designs (e.g., see refs. 1 and 2) employ a thin layer of alumina (Al_2O_3) for this purpose, which experiences temperatures of 950 to 1400 K under a impressed voltage of the order of 10 volts in series-connected arrangements. These conditions have raised some doubts as to the life of the insulator because of possible electrolysis effects (e.g., see refs. 3 to 5). Under the influence of the impressed voltage, lattice ions (Al^{+3}, O^{-2}) may move to and collect at the metallic electrode surfaces (collector and coolant pipe). Electrode oxidation, metal dendrite formation, or gas evolution could occur. These could lower the resistance of the layer, weaken the metallic/ceramic bond, or cause premature breakdown of the insulator.

Although studies of conductivity mechanisms in alumina have been made, and polarization phenomena characteristic of ionic transport have been found (refs. 4 and 6), few long-term tests have been conducted. For this reason, a test was set up using a sample with the appropriate material and geometrical characteristics in a high-temperature vacuum environment. The test was designed to maintain a relatively constant current of 3 to 4 milliamperes through the sample at a temperature of about 1325 K. Calculations indicated that if destructive effects at the electrodes occured at a rate corresponding to 100 percent ionic conduction, some effect should be evident after a few hundred hours.

SYMBOLS

A, A'	constants
E	activation energy, joules
I	current, amperes
K'	constant
k	Boltzmann constant, 1.38×10^{-23} joule/K
R	electrical resistance, ohms
R_{1325}	temperature-reduced resistance of trilayer, ohms
T	temperature, K
t	time during test, hours
V	voltage, volts
ρ	electrical resistivity, ohm-centimeters
Subscript:	
TL	trilayer

TEST APPARATUS

Trilayer

The test specimen, shown in figure 2, was a cylindrical, three-layered, fully bonded structure. Its length is about 19 millimeters and its diameter 16 millimeters.

The center alumina layer is 0.25 millimeter thick, and the niobium layers 0.38 millimeter. From the dimensions, the relation between the insulator's resistance and resistivity was calculated to be $\rho = 430\ R$, with ρ in ohm-centimeters and R in ohms.

The trilayer was fabricated using a gas-pressure bonding technique. The starting material for the insulator layer was relatively impure, containing 1.35 percent SiO_2 and 1.05 percent CaO as well as lesser amounts of Ga, Fe, Mg, Ti, Cr, B, Cu, and Mg. The major impurity in the niobium was Ta (550 ppm).

The particular sample used had undergone some measurement cycles and heating periods prior to this test. These included a series of dc resistance measurements (of short duration) and ac measurements. For 2 weeks immediately preceding the long-term test, the sample was baked out at 1275 K.

Furnace and Trilayer Support

The furnace used in the test is shown in figure 3. The heating element is a split tungsten cylinder 0.51 millimeter thick and 51 millimeter in diameter. It is resistance heated using a low-voltage dc power supply. Power to the element is manually controlled, with no automatic features. The heating element support is water cooled. Surrounding the element are five tungsten radiation shields, insulated from the furnace chamber. The chamber itself is a double-walled, water-cooled steel tank, with an opening at the top for sample installation. It is connected to the vacuum equipment, which includes an oil diffusion pump but no cold trap. The chamber pressure is measured with an ionization gage; typical pressure at 1275 K is about $2\times10^{-4}\ N/m^2$ (1.5×10^{-6} torr).

The fixture for supporting the trilayer and making electrical contact is also shown in figure 3. It consists of two U-shaped clamps supported by steel rods. Each clamp makes electrical contact with only one niobium layer (through the niobium spacer) and is insulated from the other layer (by means of the alumina spacer). A Chromel-Alumel thermocouple is suspended inside the trilayer as shown. The thermocouple and the two support rods are brought out through the top cover plate using teflon-insulated vacuum fittings. A check of the fixture showed that the resistance of the alumina spacers was greater than 10^7 ohms at 1275 K.

Electrical Circuit

A schematic of the circuit used is shown in figure 4. Variable resistor R_1 is used to adjust the current to the trilayer. Resistor R_2 prevents a high current through the trilayer; R_3 is a precision resistor used to measure the current. Resistors R_4, R_5, R_6, and R_7 form an adjustable divider network to measure and record the trilayer voltage over three decades.

PROCEDURE

Prior to the start of the test, the resistance of the trilayer measured 1.89×10^3 ohms ac (1000 Hz) and 4.50×10^3 ohms dc (6-volt bridge measurement).

For the first 5 hours of the test, the trilayer current was about 1 milliampere. During this time, the resistance decreased from 4.4×10^3 ohms to about 2.8×10^3 ohms, and appeared to be leveling out at this value. During the next hour the current was increased gradually to about 4 milliamperes, after which the resistance rose to about 7.5×10^3 ohms in 2 hours and steadied.

Trilayer current and voltage were recorded throughout the test; thermocouple output was recorded until $t = 1370$ hours, when it failed. Pressure during the test was between 1.1×10^{-4} and 1.3×10^{-3} N/m^2 (8×10^{-7} to 10^{-5} torr measured), except for the 4-hour period between $t = 168$ and $t = 172$ hours. During this time the diffusion pump heater was off and the pressure was about 1.3×10^{-1} N/m^2 (10^{-3} torr measured).

The trilayer was subjected to a dc current of 2.6 to 4.0 milliamperes for a total of 3010 hours, except for three short periods in the first 150 hours. At these times, ac resistance measurements were taken; the values were all about equal and slightly below the pretest value.

RESULTS AND DISCUSSION

Test conditions (temperature, voltage, and current) and trilayer resistance during the test are shown in figure 5.

As shown in the figure, temperature during the first 1400 hours of the test was between 1295 and 1335 K, with one exception. This was an unexplained rise from 1325 K to 1375 K between $t = 200$ and $t = 380$ hours. The furnace power was then adjusted to return to 1325 K. Two changes in the furnace power supply setting were made after the thermocouple failure: a small increase at $t = 1658$ hours, and a larger one at $t = 2214$ hours. Based on a correlation of the power supply control setting with temperature from previous data, these adjustments resulted in temperature rises to about 1340 and 1375 K, respectively. An error of ±5 K (maximum) must be associated with each temperature point, based on comparisons between printout data and more precise potentiometer measurements. In addition, during certain periods of erratic recorder behavior, an error of -0K, +10 K must be added to the ±5 K. These periods were from 265 to 505 hours, and from 1034 to 1152 hours.

The trilayer current remained relatively constant (2.6 to 4.0 mA) during the test, as intended. Thus the voltage followed changes in the trilayer resistance. A rough integration of the current over the total test period (3010 hr) showed that about 3.4×10^4 coulombs of charge passed through the trilayer. This is about six times the charge originally present in the form of O^{-2} or Al^{+3} ions.

The trilayer resistance during the test is also shown in figure 5. The decline in resistance from 0 to 200 hours is not due to a temperature rise. If anything, the temperature dropped during this period. A change in the materials' conductivity seems to be occurring. The larger drop in resistance between 200 and 350 hours is a temperature-induced change, however. This is borne out by the fact that the resistance returned to its original value (about 4 kilohms) when the temperature was lowered to its original value. The large rise in resistance beginning at about 750 hours may be partly due to a temperature drop. However, the resistance increase was far too large to be due to temperature alone. A slight drop in temperature occurred between 750 and 900 hours, but thereafter the temperature rose, mainly due to three small adjustments of the furnace power supply. After reaching a maximum value of about 20 kilohms near 1600 hours, the resistance remained relatively steady through the end of the test. The drop near 2200 hours was due to the fairly large temperature adjustment mentioned earlier.

In order to get a better idea of the resistance change independent of temperature changes, a "reduced resistance" was calculated for various R_{TL} values, and is plotted in figure 6. This reduced value, R_{1325}, is the calculated resistance the trilayer would have at 1325 K. The procedure used to calculate R_{1325} is as follows:

Assuming the resistivity can be expressed as

$$\frac{T}{\rho} = Ae^{-E/kT}$$

where $\rho_{TL} = K'R_{TL}$ and K' is a geometrical constant, then

$$R_{TL} = A'T_{TL}e^{E/kT_{TL}}$$

and

$$R_{1325} = A'(1325\ K)e^{E/k(1325K)}$$

Dividing these equations and solving for R_{1325} yields

$$R_{1325} = \frac{1325\ K}{T_{TL}} R_{TL} e^{E/k\left[(1/1325)-(1/T_{TL})\right]}$$

Thus the resistance at 1325 K can be calculated from R_{TL} at any temperature if the energy E is known. For figure 6, a value of 3.7×10^{-19} joule (2.3 eV) was used. This was the value obtained from a series of points taken between 150 and 264 hours (curve IV in fig. 7). Figure 6 shows the slight drop in resistance at the beginning of the test (the point at $t = 0$ represents the pretest dc bridge resistance). It also indicates that most of the drop in R_{TL} between 200 and 350 hours is due to temperature. Evidently the large rise in resistance began at about 950 hours; the increases prior to this (750 to 950 hr) were due to temperature changes. The last point for which a temperature reading was obtained (1370 hr) shows that a fourfold increase in the true resistance occurred after 950 hours.

Figure 7 shows some plots of T/R_{TL} against reciprocal temperature for various times. Curves I, II, and III were obtained several months prior to the 3000-hour test, while curves IV and V represent values during the test. The activation energy E obtained from the slope of the line is given for each set of points. It should be noted that the temperature ranges involved are relatively small, and the E values are very sensitive to temperature differences. Thus, at least for the dc curves (III, IV, and V), the differences in E are probably not significant.

After the furnace was shut down at $t = 3010$ hours, the trilayer dc resistance rose steadily to about 10^6 ohms; loss of sensitivity prevented further dc measurements down to ambient temperature. An ambient-temperature ac value was obtained, however. It was 3.4×10^8 ohms, or about 10 times the pretest value.

Except for a shiny, "etched" appearance on the surface of the niobium, no visual changes in the trilayer were apparent. Examination of the insulator and bonds at ×30 magnification also revealed no changes.

A transverse section through the center of the trilayer was prepared, and is shown in figure 8. For comparison, figure 9 shows a section of an unbonded tube of the same material which did not undergo any testing. Some of the differences in the two samples, such as grain boundary prominence, may be due to different polishing methods. However, the grain pullout during metallographic preparation in the test sample is much more severe, indicating some weakening of the grain boundaries. The area shown in figure 8 is typical of the entire section, in that most of the pullout occurred near the outer niobium layer. This was the electrically positive layer in the test. In addition, the appearance of the niobium/alumina bond is different at the outer and inner layers.

This is shown in greater detail in figure 10. The outer niobium had many areas which appeared to be interlocked with the insulator. Figure 10(a) is typical of this. The inner layer, on the other hand, had no such interlocking (see fig. 10(b)). Instead, there was a thin layer of material (darker than the alumina) between the metal and insulator.

Electron microprobe scans at ×500 showed fairly sharp niobium and aluminum bond areas. If any interdiffusion had taken place, it was at most only about 3 micrometers. The scans showed a large concentration of silicon at both boundaries. It looked as if there was more silicon in the 10 micrometer layers at the boundaries than in the body of the insulator. Calcium, on the other hand, was seen mainly in the body of the insulator, and looked evenly distributed. Although there was a considerable amount of calcium at the inner boundary, there was none at all at the outer. This indicates that the second phase at the inner boundary (fig. 10(b)) is probably calcium.

A deposit which formed on the glass surface of the viewing port (see fig. 2) was spectrographically analyzed. The major constituents were the elements in stainless steel, along with lesser amounts of tungsten and tantalum. Aluminum was listed as "very weak."

It is interesting to compare the results of this test to those of Chin and Messick (ref. 7). Their niobium/alumina bonded trilayer was quite similar in dimensions, but a higher purity alumina (Lucalox) was used. Thus the resistance of their sample was about 50 times that of the trilayer described in this report. In addition, their test conditions were 100 volts dc at 1500 K for 5313 hours. The sample resistance increased by a factor of 50 during the test period, and drastic changes were seen in the structure. The alumina was completely broken up at the outer (positive) layer. Diffusion of aluminum into the inner niobium extended about 30 micrometers.

Although the amount of charge that passed through the Chin-Messick sample was only about one-tenth that of the trilayer described herein, the damage done was much more severe in their case. This is probably because the total ionic charge transport was larger for their sample. A large proportion of the current through the trilayer of this report must have been electronic (and thus nondestructive) in nature. This is probably because of the large amounts of impurities.

It should be pointed out that the radiation environment of an in-core thermionic system may produce quite different results than those seen in an out-of-core test.

SUMMARY OF RESULTS

A bonded alumina trilayer was tested for 3000 hours under the following conditions: (1) a continuous dc current of about 3 milliamperes, (2) a voltage of 15 to 50 volts for most of the test, (3) a temperature of about 1325 K, and (4) a pressure of about 1.3×10^{-4} N/m^2.

The overall change in resistance was a fivefold increase, most of it occurring during the middle third of the test. Although no change in the general appearance of the sample was seen, a possibility of niobium-alumina reaction was noted in photomicrographs. In addition, significant grain pullout occurred at the positive side of the insulator. However, electron microprobe scans showed little niobium or aluminum interdiffusion.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 19, 1971,
120-27.

REFERENCES

1. Anon.: Proceedings of the Thermionic Conversion Specialist Conference. IEEE, 1968.

2. Anon.: Proceedings of the Thermionic Conversion Specialist Conference. IEEE, 1969.

3. Davies, Myron O.: Transport Phenomena in Aluminum Oxide. NASA TN D-2765, 1965.

4. Tallan, N. M.; and Graham, H. C.: Interfacial Polarization and Electrical Conductivity in Sapphire. J. Am. Ceram. Soc., vol. 48, no. 10, Oct. 21, 1965, pp. 512-516.

5. Vest, R. W.; and Tallan, N. M.: High-Temperature Transference Number Determinations by Polarization Measurements. J. Appl. Phys., vol. 36, no. 2, Feb. 1965, pp. 543-547.

6. Cohen, J.: Polarization Effects in Electrical "Conductivity" of Artificial Sapphire at High Temperatures. J. Phys. Chem. Solids, vol. 16, no. 3/4, 1960, pp. 285-290.

7. Chin, J.; and Messick, C. W.: Thermal Stability Testing of an Electrically Loaded Sheath Insulator. Proceedings of the Thermionic Conversion Specialist Conference. IEEE, 1969, pp. 394-403.

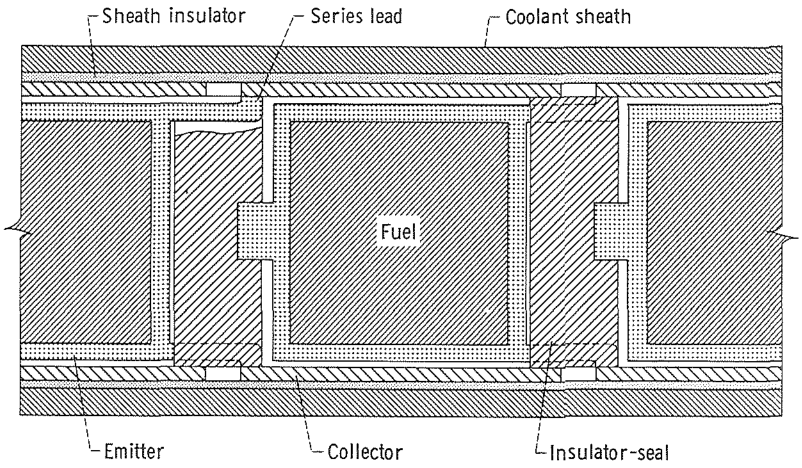


Figure 1. - Typical in-core thermionic fuel element.

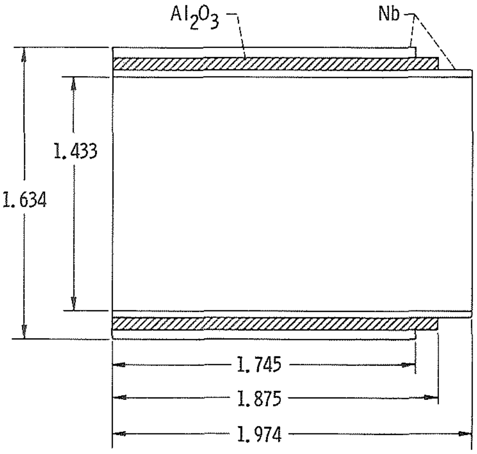


Figure 2. - Trilayer test specimen. Niobium layers, 0.38-millimeter thick; alumina layer, 0.25-millimeter thick. Dimensions are in centimeters.

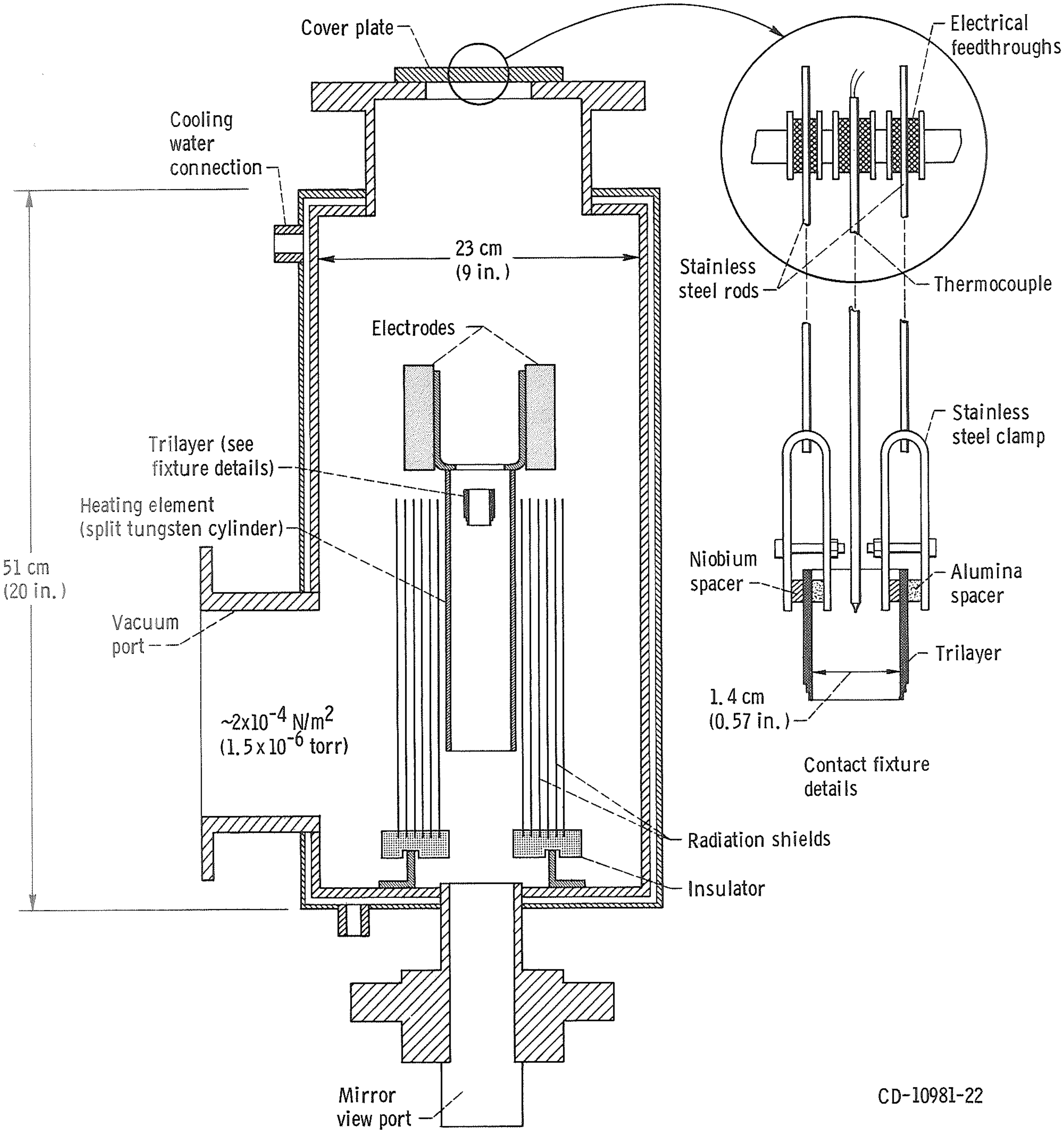


Figure 3. - Vacuum furnace and contact fixture.

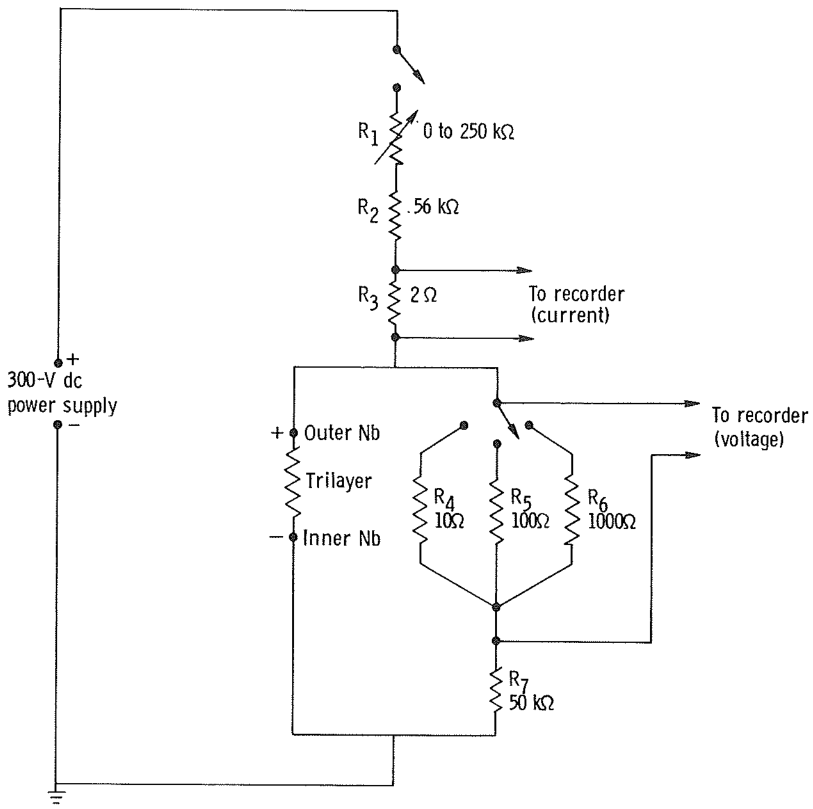


Figure 4. - Electrical circuit.

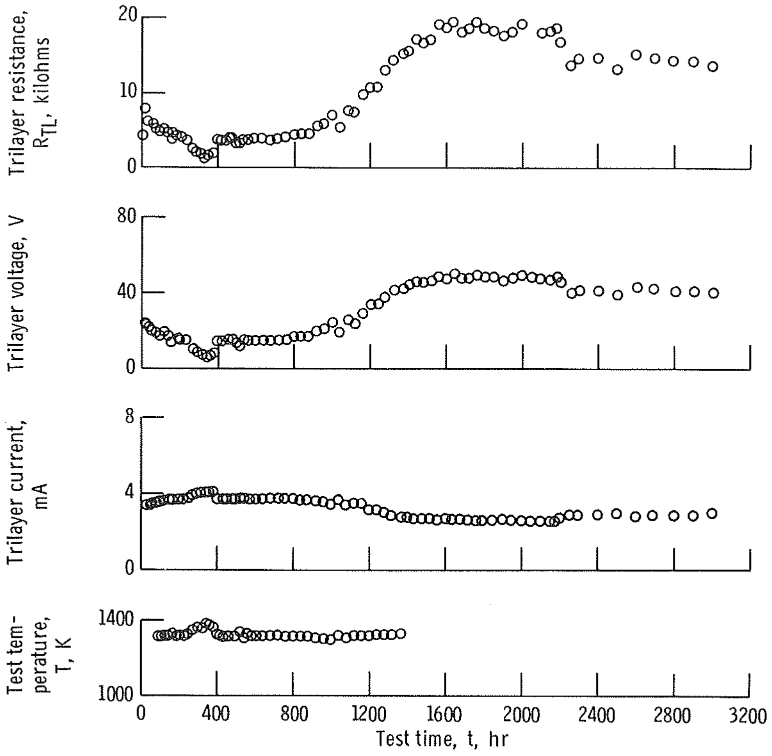


Figure 5. - Test conditions (temperature, current, voltage) and trilayer resistance.

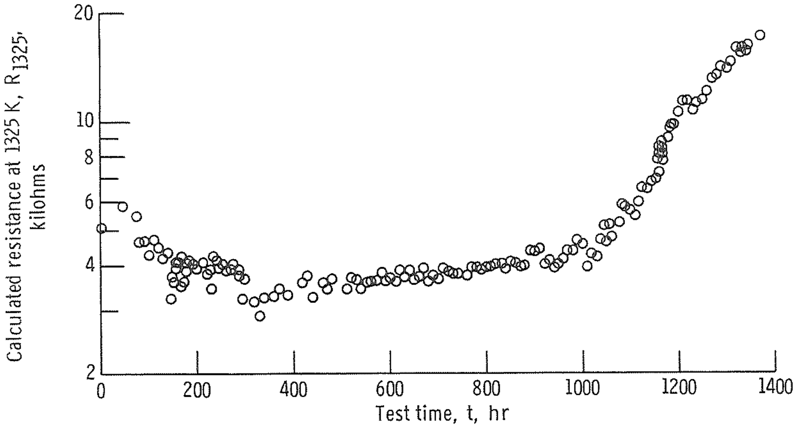


Figure 6. - Calculated "reduced" resistance.

Curve	Type of measurement	Time, t, hr	Activation energy, E, J	(eV)
I	ac	Pretest	2.5×10^{-19}	(1.6)
II	ac	Pretest	2.2	(1.3)
III	dc	Pretest	3.2	(2.0)
IV	dc	150 to 264	3.7	(2.3)
V	dc	1345	3.4	(2.1)

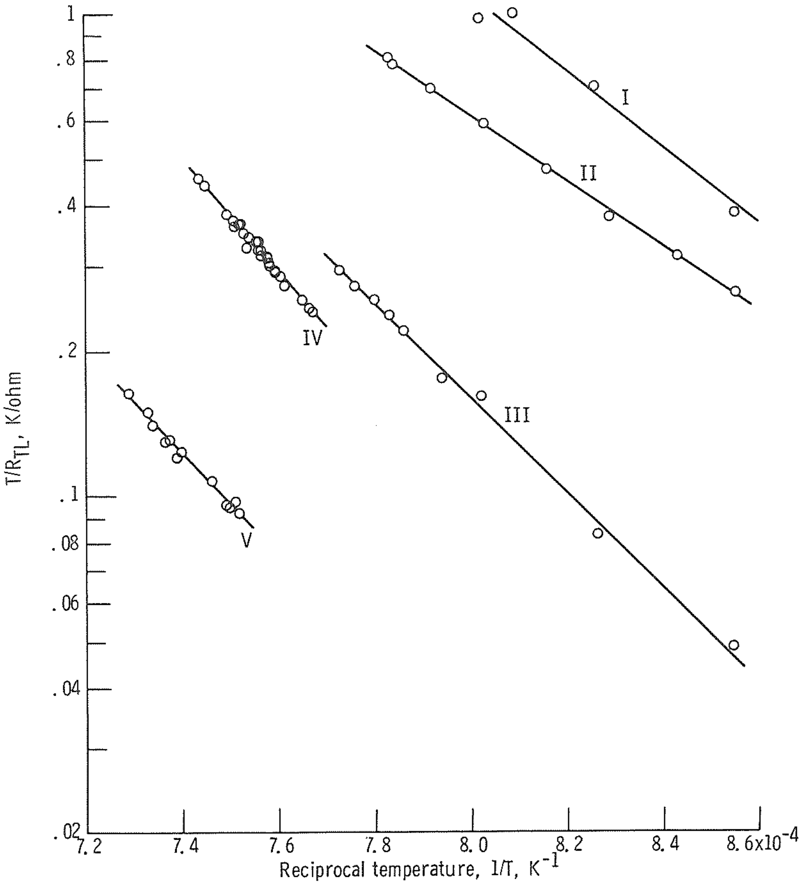


Figure 7. - Activation energy curves for trilayer before and during test.

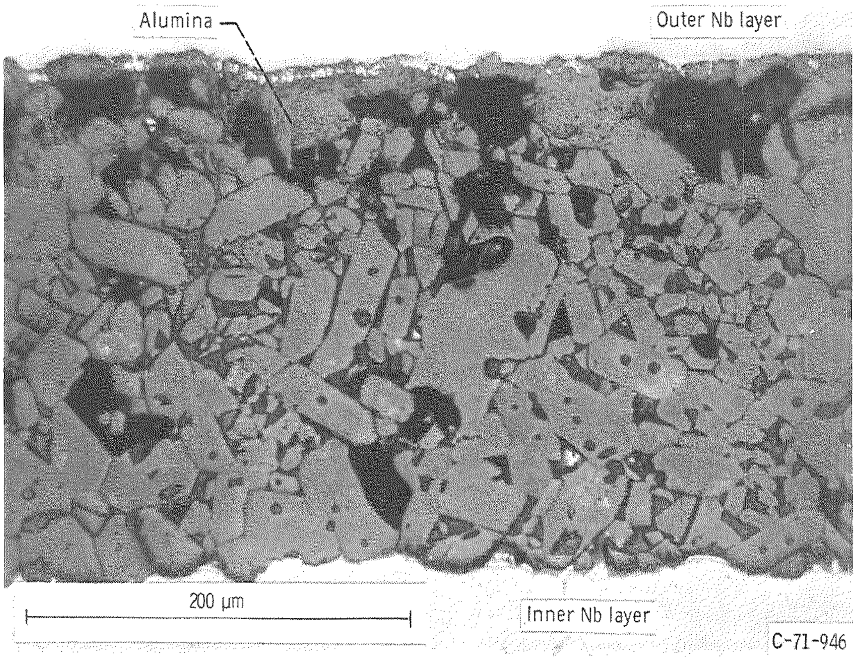


Figure 8. - Photomicrograph of trilayer after 3000-hour electrical test. Unetched, X250.

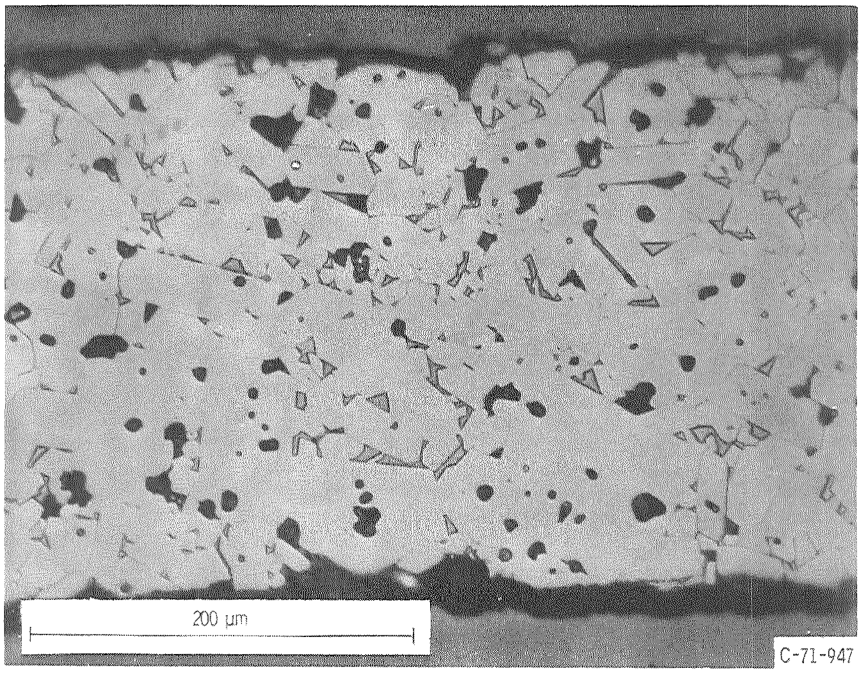
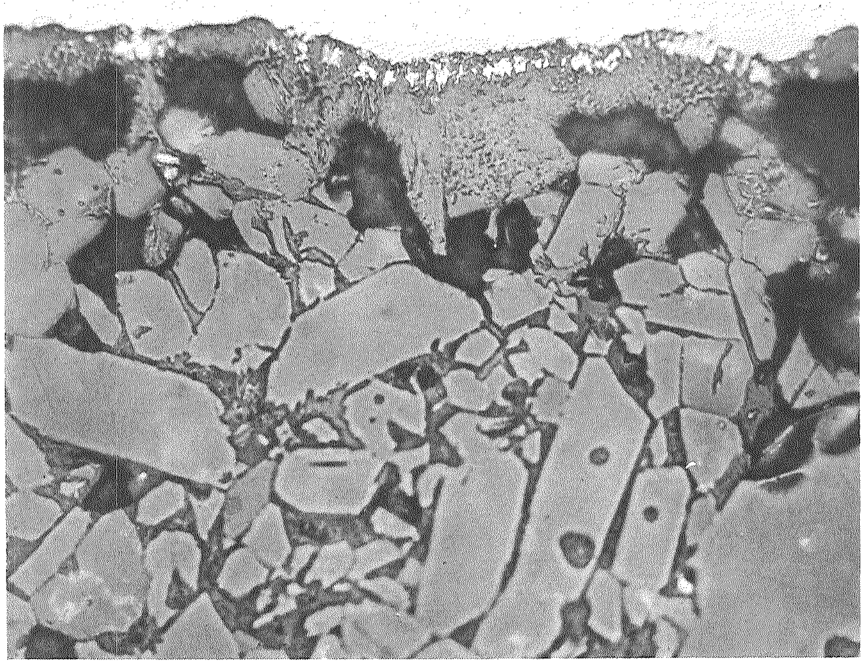
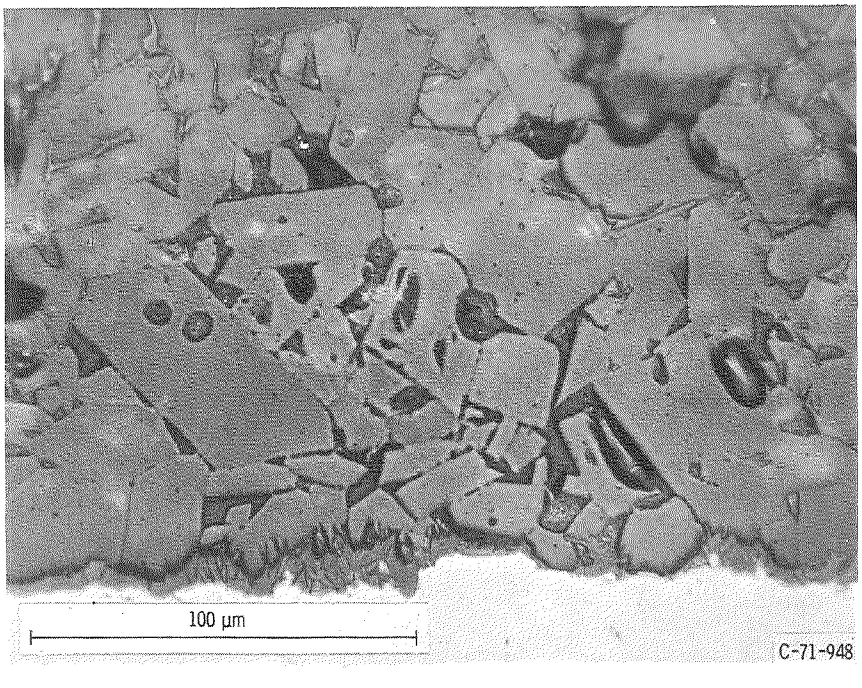


Figure 9. - Photomicrograph of alumina tube of same material used in test trilayer. Unetched, X250.



(a) Outer niobium interface.



(b) Inner niobium interface.

Figure 10. - Photomicrographs showing detail at niobium/alumina boundaries. Unetched, X500.

> *"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*
>
> —NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546