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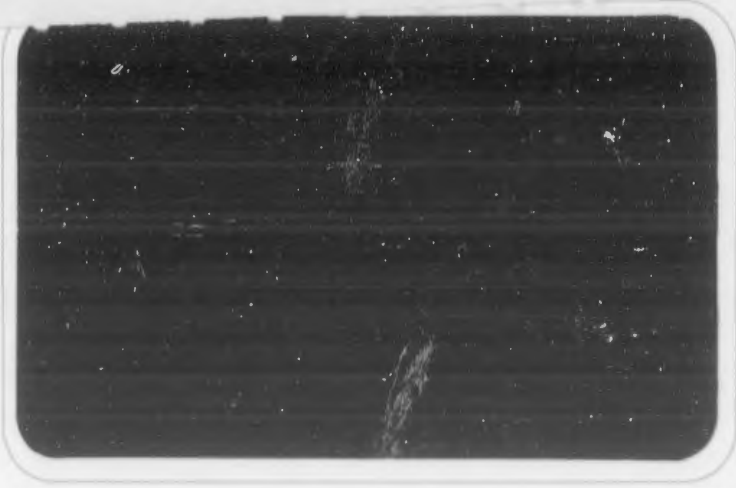


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Westinghouse

ELECTRIC CORPORATION

AEROSPACE ELECTRICAL DIVISION

ALKALI METAL RESISTANT WIRE

USAF CONTRACT AF33(657)10701

PROJECT NO. 8128

TASK NO. 8128-08

WESTINGHOUSE ELECTRIC CORPORATION

AEROSPACE ELECTRICAL DIVISION

LIMA, OHIO

February 15, 1964

This Quarterly Report covers the period November 15, 1963, to
February 15, 1964, on Contract AF33(657)10701, Task No. 8128-08.

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NOTICE

The work covered by this report was accomplished under Air Force Contract AF33(657)10701, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings and conclusions contained herein. It is published for the exchange and stimulation of ideas.

**DEVELOPMENT OF HIGH TEMPERATURE
ALKALI METAL RESISTANT INSULATED WIRE**

**4th Quarterly Progress Report
Contract AF33(657)10701, Task No. 8128-08**

February 15, 1964

**Westinghouse Electric Corporation
Aerospace Electrical Division
Lima, Ohio**

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FOREWORD

This report is submitted by the Aerospace Electrical Division, Westinghouse Electric Corporation, Lima, Ohio, on Air Force Contract AF33(657)10701, Task No. 8128-08, "Development of High Temperature Alkali Metal Resistant Insulated Wire". The contract is administered by the Aeronautical Systems Division, Wright Patterson Air Force Base, Dayton, Ohio. Mr. Lester Schott is project engineer.

The work described in this report was carried out by personnel at the Research and Development Center, Department of Insulation and Chemical Technology, Westinghouse Electric Corporation, Pittsburgh, Pennsylvania.

ABSTRACT

This report covers the progress during the fourth quarter on Air Force Contract AF33(657)10701. The program effort is directed toward the development of an insulated electrical conductor resistant to saturated potassium (850 C) and mercury (538 C) vapors. Thirty-three samples were exposed to potassium vapor at 850 C. Six samples were exposed to mercury vapor at 540 C. Preformed coils of nickel clad silver were coated with molybdenum and nickel aluminide respectively by plasma-arc spraying techniques. These coils were then insulated by plasma-arc sprayed coatings of zirconia (99%), followed by high purity alumina (98%). Vibration, shock, acceleration, and humidity tests were conducted on these insulation combinations in a statorette. These tests were successfully passed by the insulated wire.

An attempt was made to measure the leakage resistance of a sapphire to tantalum seal while the seal was exposed to potassium vapor at 850 C. This attempt was partially successful. The results of this test indicate potassium vapor at 850 C will not act as a conductor.

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I. INTRODUCTION

Rotary power sources for advanced weapon systems based on nuclear reactors as energy sources utilize liquid metals as the working fluid to drive the turbines. Since the a-c generator used to supply the electrical energy is attached to the turbine shaft, its electrical insulation would be exposed to any of the metal vapor leaking through the seals. Present electrical insulation will probably be severely attacked when exposed to high temperature mercury vapor or alkali metal vapor such as potassium. In order to provide reliable electrical power, the present insulation must be protected from metal vapor by stator canning techniques.

Under this contract, a program was initiated to investigate insulation materials, electrical conductors, and coating methods needed in the development of a high current (4000 amps per square inch) round wire for advanced electromagnetic alternators that are exposed to mercury and alkali metal vapors. Saturated mercury vapor at 538 C was chosen to provide a realistic vapor pressure in test cells. Saturated potassium vapor at 850 C was chosen as a representative alkali metal vapor condition. The design objective life of the insulated conductor in the metal vapor environment is 10,000 hours. The electrical resistance of the conductor at test temperature during its life is not to exceed 150% of the copper standard at 850 C. The room temperature tensile strength of the conductor

is to be in excess of 30,000 psi. The initial purity of the potassium used in the exposure tests is 99.97%.

It is preferred that the conductor be insulated with a compatible high temperature insulation that is resistant to metal vapor attack, however, if this is not possible, then a potting compound compatible with the insulation and resistant to the metal vapor will be evaluated. The electrical strength from conductor to ground should have a design objective of 1200 volts. If the insulated conductor is potted, the electric strength of the insulation should be at least 300 volts per mil.

The final evaluation of the insulated wire will be done in statorettes. The insulated conductor coils will be inserted in test statorettes to investigate the effect of test environments. While in the statorette, the insulation system will be subject to metal vapors, temperature, thermal shock, nuclear radiation, vibration, mechanical shock, humidity and acceleration.

II. SUMMARY OF WORK PERFORMED DURING THE QUARTER

1. Thirty-three sample exposures to potassium vapor at 850 C and six sample exposures to mercury vapor at 540 C were completed during this quarter. Uncoated Ni clad Ag wire and flame sprayed zirconia (Metco 201) coatings over nickel aluminide coated nickel clad silver wire appeared unaffected by the 172 hours exposure. One of the coated samples had an aluminum nitride overcoat on the zirconia coating. A Lucalox to niobium joint made with an alumina-calcia glass also appeared unaffected by the exposure. Aluminum nitride overcoated Metco 105 alumina on Oxalloy 28 and a plasma sprayed alumina coating over molybdenum coated nickel clad wire were badly cracked and lifted after exposure to potassium. An Alite 610 alumina body brazed (OFHC Cu) to A nickel and overcoated with a nickel plate was also badly attacked by potassium vapor.
2. All of the brazing alloys exposed to mercury vapors at 540 C were unaffected by the 100 hour test exposure. The Ni-Ti brazing alloys appeared relatively unaffected by 170 hours exposure to potassium vapor at 850 C; however, a Lucalox-Ta joint made with the 72% Ti-28% Ni alloy parted at the interface during potassium vapor exposure.

3. A test capsule consisting of a tantalum tube and sapphire disc was charged with potassium and the electrical leakage resistance of the sapphire was measured at temperatures to 850 C. At 850 C, a value of 9.1×10^4 ohms was measured compared to 5.7×10^7 ohms when the capsule contained only argon. The actual concentration of the metal vapor in the capsule is not known since there were indications the tantalum Swagelok used to seal the capsule began to leak at 450 - 500 C.
4. Use of nickel aluminide as an undercoat significantly improved the adhesion of various oxides to the nickel clad silver wire.
5. The shipment of Inconel clad silver wire was received from Sylvania on 2 January 1964.
6. Adherent aluminum nitride coatings could not be applied directly to nickel, Inconel, or stainless steel substrates, however, they were successfully formed at 800 C as overcoats on plasma sprayed zirconia (Metco 201) coatings on nickel clad silver wire. A nickel aluminide substrate had been used under the zirconia coating. The aluminum nitride coating remained intact on only one of the three samples after storage in the laboratory. An electrical leakage resistance at 850 C in argon of 1.8×10^4 ohms was measured on the multi coat insulation. The leakage resistance of

the zirconia coating without the AlN overcoat was only 5 ohms at 600 C.

7. Adherent AlN coatings were successfully formed directly on molybdenum and tungsten substrates. The electrical leakage resistance of a thin AlN coating over a Mo rod at 850 C in argon was 4.0×10^5 ohms.
8. The electrical leakage resistance of a reinforced Alite C-500 cable end seal on a Hg charged stainless steel capsule was determined. A value of 1.5×10^8 ohms was measured (insulator at 425 C - Hg reservoir at 405 C) before a vapor leak developed. Extrapolation of the data to 540 C for this degree of Hg vapor saturation gives a value of 10^6 ohms.
9. The electrical leakage resistance in argon was determined on a capsule formed by sealing niobium end caps to a Lucalox tube with an alumina-calcia glass. A value of 2.2×10^7 ohms was measured at 850 C.
10. High purity strontium zirconate powder was obtained from The Zirconium Corporation and was successfully plasma sprayed onto wire. The coating lost its adhesion to the wire substrate after a 170 hour exposure to potassium vapor at 850 C.

11. Preformed coils of Ni clad Ag wire were successfully plasma sprayed with an adherent, uniform, one mil coating of zirconia. Zirconia, alumina, and magnesia were plasma sprayed on Inconel strips and on short lengths of Ni clad Ag wire on which the ends had been sealed with a seven mil electroplate of Ni. Only the zirconia (Metco 201) coatings over NiAl coated substrates maintained excellent adhesion after 170 hours exposure to potassium vapor at 850 C.
12. Leak tight joints were successfully made between tantalum and stainless steel tubes using Microbraz 30 and 130.
13. Four additional leak tight lead-in units (Ta tube, sapphire disc, .030" Ta lead wire) were made using the 95% Zr-5% Be brazing alloy. On repeated thermal cycling, all units developed cracks in the sapphire at the lead-in wire, due to differential thermal expansion.
14. Successful Ta tube-sapphire disc-Ta wire lead-in units could not be made with either the aluminum silicate glass or the 28% Ni-72% Ti brazing alloy.
15. Two insulated preformed coils of Inconel clad Ag wire were sent on 10 February 1964 to the Brookhaven National Laboratory for exposure to nuclear radiation. Plasma sprayed NiAl and

molybdenum were the respective undercoats for the insulation. One coil was plasma sprayed with strontium zirconate and the other with Metco 201 zirconia overcoated with Metco 105 alumina. Molybdenum, plasma-arc sprayed, was the undercoat in the latter coating.

16. Six test statorettes were fabricated from four mil Hiperco punchings.
17. Fifteen preformed coils were made of nickel clad silver conductor (.128" O.D.). Three of these coils were then layer coated by means of plasma-arc spraying technique. The composition of these coatings are as follows.
 1. A two mil coating of molybdenum followed by a three mil coating of 99% alumina.
 2. A two mil coating of molybdenum, two mil coating of alumina and finally a two mil coating of zirconia.
 3. A two mil coating of nickel aluminide, two mil coating of 99% zirconia (Hafnium free). The final coat was two mils of alumina (99%).
 4. A two mil coating of molybdenum, two mil coating of zirconia, followed by a two mil coating of alumina (99%).
18. A potassium vapor test capsule with two ceramic^{insulated} terminals has been constructed for the ceramic insulated wire tests in a statorette subjected to 850 C potassium vapor.

19. Vibration, shock, acceleration, and humidity testing was conducted on a ceramic insulated coil wedged in a stator-ette. The insulation coating remained intact.

III. EXPERIMENTAL WORK AND EVALUATION OF RESULTS

3.1 Metal Vapor Exposure - Mercury and Potassium

Thirty-three sample exposures to potassium vapor at 850 C and six sample exposures to mercury vapor at 540 C were completed during this quarter. The listing of the specimens, the weight changes measured and the visual observations after exposure are contained in Tables 1 and 2.

In addition to the above work, two more attempts were made to achieve a leak tight stainless/tantalum joint using a stainless Swagelok on a tantalum tube. In the first experiment, tantalum ferrules were substituted for those of stainless steel tried initially. The system again leaked as a temperature of 400 C was reached.

All fittings of each Swagelok were then heavily coated with the Silver "Goop" recommended by Crawford Co. This offered no improvement in the upper temperature limit of the system.

A series of capsules containing a ceramic cable connector, Alite C-500, were also prepared and charged with mercury. These capsules were used in resistivity measurements trials.

3.2 Electrical Tests

3.2.1 Testing in an Argon Environment

3.2.1.1 Pre-Metal Vapor Exposure Measurements on Test Capsules

Electrical leakage resistance measurements were made in argon on a tantalum tube sealed with a Lucalox disc and three tantalum tubes sealed with sapphire discs. The tantalum tubes, open at one end, were 1-1/2 inches long and 1/2 inch in diameter. The Lucalox disc and one sapphire disc were 1/16 inch thick and the second sapphire disc was 1/8 inch thick. In all four cases, the brazing alloy was a 95% zirconium-5% beryllium combination, brazed at 1035 C under vacuum conditions. A 1/32 inch diameter tantalum pin extended through and was brazed to the center of each disc. A very thin film of nickel was plated on the tantalum tube with the Lucalox disc. This was done to check on possible improvement in the resistance of tantalum to oxidation and, in later tests, to potassium vapor corrosion.

Figure 1 contains the temperature-electrical resistance characteristics measured for the tantalum-Lucalox capsule as its temperature was raised. The "first trial" measurements (9×10^5 ohms at 500 C) were so low it was decided not to heat the capsule to 850 C. Measurements of electrical leakage resistance, upon lowering the capsule's temperature, were considerably lower than the corresponding temperature points (1.4×10^8 ohms at 25 C). After this test, the Lucalox ceramic was sand-blasted to remove the relatively

high conducting condition presumed on its surface. The "second trial" electrical measurements were made to a temperature of 540 C. Higher values of resistance were found. Once again, however, with decreasing temperature, the measured electrical resistance of the capsule was noted to be considerably lower than the increasing temperature values.

The low electrical leakage resistance measured during the first trial may be attributed, in part, to the effects of the nickel plating solution on the insulator surface. It may also be possible that some metal is being condensed on the test sample from the copper tube which is employed to distribute the furnace heat more uniformly inside of the Vycor combustion tube.

Prior to making further electrical measurements, a number of modifications and changes were made in the argon supply and the test apparatus. This work was done to eliminate suspected undesirable conditions imposed on samples previously tested. An attempt has been made to improve on the purity of the tank argon used. First, argon was made to pass through an activated alumina dryer to absorb moisture. Next, dry argon flowed over closely packed fine copper wire at a temperature favoring deoxygenation of the gas. Finally, dry deoxygenized argon was forced through a

flowmeter prior to entering the combustion tube-electrical resistance measuring apparatus. The rubber stopper previously used at the downstream end of the Vycor tube was replaced with glass. An exit for the argon gas was provided through a 9mm glass tube with a 90° upward bend partially closed to form a nozzle. The end of the nozzle is well above the top of the Vycor combustion tube. In addition to eliminating the rubber stopper, this modification reduced back diffusion of room air and permitted more complete purging of residual air from the combustion tube.

Figure 2 contains the temperature-electrical resistance characteristics measured for two of the tantalum-sapphire capsule seals. The resistance of capsule seal #1 at room temperature "as received" was about 1300 ohms. The resistance-temperature characteristics shown for seal #1 in Figure 2 was obtained after sand blasting its sapphire surfaces. The "as received" electrical characteristics of the third sapphire unit are presented on Figure 3. The value measured at 850 C (5.7×10^7 ohms) compares favorably with the value (9.7×10^7 ohms) previously measured on a 1/16" thick, 1/2" diameter sapphire disc.

The resistance-temperature curve for capsule seal #2 is about 2-1/2 decades higher than that of seal #1. It will be noted, however, that as the temperature of seal #2 was

lowered, its electrical resistance remained very low (about 10^5 ohms at 400 C). It is possible that this characteristic was due to thermal degradation of a rubber stopper used to construct the argon gas flow at the upstream end of the Vycor tube. As indicated above, this stopper was later replaced with a glass stopper.

A sapphire disc with a tantalum wire penetration was brazed with the Zr-Be alloy into the I.D. of the tantalum end of one of the Ta/SS tube units. The joint remained leak tight on thermal cycling to 850 C. The electrical leakage resistance of the sapphire in argon was measured at temperatures up to 850 C and found to be about one order of magnitude lower than that of previously tested samples. At 850 C, a value of 1.9×10^6 ohms was measured. Post examination of the unit showed that the sapphire disc had cracked during electrical the/test run and the capsule was no longer leak tight.

3.2.1.2 Pre and Post Metal Vapor Exposure Measurements on Coatings

Electrical measurements on a 1/8-inch diameter nickel rod sprayed with Metco 201 zirconium oxide were conducted in an argon atmosphere to a temperature of 850 C. The average total build of zirconia was 12 mils on the 2 $\frac{1}{4}$ -inch long nickel rod. An outer sheath electrode, 3/4-inch long, was made by closely winding 5 mil diameter nickel wire helically

around the zirconia insulated nickel rod. The measured leakage resistance of the zirconia sample is shown in Figure 4. Electrical measurements were discontinued after the sample resistance had decreased to near 5 ohms at 600 C. The measuring voltage (240 volts d-c) imposed a gradient across the zirconia wall of 40,000 volts per inch. Even though this gradient does not appear too high, a second zirconia insulated nickel rod sample was tested at a lower circuit voltage (5-6 volts); however, an identical electrical leakage resistance value was measured.

An insulated helical coil (3/4" dia x 1 1/2" long) of Ni clad Ag wire was next tested. An AlN overcoat had been formed over a plasma sprayed (1-2 mil) Metco 201 zirconia coating on a 1 to 2 mil Metco 404 NiAl undercoat. The AlN coating had been formed at 800 C. A resistance value of 1.77×10^4 ohms was measured in argon at 850 C. The data measured over the entire temperature range is shown in Figure 5. Measurements were made at 23 volts (4.6 volts at 850 C) because the initial 300 volts applied potential caused breakdown of the coating.

Attempts to measure the electrical leakage resistance of sample WK-18 (same construction as above but exposed to potassium vapor) were unsuccessful. The room temperature value was about 1.5 ohms and remained that value up to

850 C. Aging the sample at 900 C for several hours in argon caused a change in color from deep purple to light grey-purple, however, no change in resistance value was measured. The surface of the insulation was made conducting by the silver core loss during the potassium vapor. Other AlN samples in potassium vapor where no Ag was present did not have the conductive purple coating.

The electrical leakage resistance of a thin AlN coating on a 3/16" diameter Mo rod was measured in argon at temperatures up to 850 C. At 850 C, the measured value was 4.0×10^5 ohms. The data over the entire temperature range is shown in Figure 6. At 700 C, a white deposit with a bluish fringe started to form at the cool end of the Vycor tube. By the time the specimen temperature reached 850 C, the deposit became a dark brown. This may have been due to either slight oxidation of the Mo rod to MoO_3 (white) and the further oxidation of the deposit to Mo_2O_3 (brown) or to loss of $\text{AlCl}_3 \cdot \text{Nit}_3$ impurities in the AlN coating.

3.2.1.3 Special Lucalox Tube - Niobium End Cap Capsule

Electrical leakage resistance measurements were made on a cylindrical capsule constructed from a Lucalox tube sealed with discs of niobium using an alumina-calcia glass. A small open tube of niobium, with a Kovar extension, is

brazed to one niobium end disc. The Lucalox cylinder is 3-1/2 inches long between metal discs, 5/8 inch O.D., and 1/2 inch I.D. This Lucalox-niobium capsule was prepared by the Ceramics Section at Westinghouse R & D Center.

Results of electrical leakage resistance measurements on the Lucalox-niobium capsule are shown in Figure 7. Measurements of resistance were made as the capsule was heated to 850 C and then cooled. An electrical leakage resistance of 2.2×10^7 ohms was measured at a temperature of 850 C. The temperature was measured with a thermocouple in contact with the upstream end of the alumina tube. It is noted that the resistance measured on cooling is somewhat higher than those of the heating curve at corresponding temperatures. This is probably due to pre-evaporation of foreign materials from the alumina surface which were carried out by the argon stream.

3.2.2 Test in Mercury Vapor

Electrical leakage resistance measurements were made on two Alite C-500 cable-end terminal capsules while heated in an atmosphere of tank argon. In the first case, the Kovar flange at the top of the ceramic metal seal was reinforced on the outside with a heavy heliarc bead. This capsule was charged with mercury and sealed with a stainless steel "Swagelok" fitting. The second capsule was neither

charged with mercury nor sealed but the inside surface of the metal-ceramic seal was lined with a glass composition. The above two modifications were made to improve on the capsules' ability to resist mercury attack.

The electrical resistance-temperature measurements are shown in Figure 8. Over the temperature range plotted for the Hg charged capsule, the Hg reservoir remained a constant 20 C cooler than the insulator. The average capsule temperature is plotted, i.e., the value shown at 415 C was obtained while the insulator was at 425 C and the reservoir at 405 C. The mercury charged capsule developed a leak near 500 C. Inspection revealed that although the reinforced flange sustained mercury attack, the brazed metal-ceramic joint did not. Three individual test runs were made on the glass lined capsule. The curve representing this uncharged-glass lined capsule is an average for the three sets of resistance-temperature determinations. There is appreciable scatter in the data and the electrical resistance is relatively low at 540 C (10^6 ohms). As noted previously, but not shown on the curve, the resistance of the uncharged capsule, upon cooling, did not follow the increasing temperature curve, but was substantially lower. It is suspected that the low resistance is due to condensed metal on the ceramic portion of the capsule seal from the copper leads inside the combustion tube.

3.2.3 Tests in Potassium Vapor

One of the tantalum tube-sapphire disc test capsule described in Section 3.2.1.1 was charged with 1 cc of potassium and sealed with a Swagelok fitting fabricated from tantalum. Due to the position of the capsule during charging, the surface of the sapphire disc was covered with liquid potassium and apparently remained "wetted" by the potassium when the capsule was inverted. The resistance of the charged capsule measured about 4 ohms at room temperature. Holding the tube vertical with the sapphire end uppermost and heating to 100 C to remove the potassium coating was unsuccessful and the resistance value remained at 4 ohms. The capsule was placed in a Vycor tube and slowly heated in an atmosphere of purified argon to a temperature of 850 C. The electrical leakage resistance of the sapphire was measured during the increase in temperature. Near 500 C, a white deposit started to form on the inside of the section of Vycor tube extending beyond the tube furnace. Opening of the tube furnace, to view the test capsule, revealed a white film building up on the Vycor tube opposite the Swagelok fitting. The tantalum Swagelok apparently started to leak at a temperature only slightly higher than the previously tested tantalum tube/type 316 stainless steel Swagelok joint. The deposit on the cool end of the Vycor tube continued to build up until the capsule temperature

reached 850 C. As the capsule temperature was raised from 750 to 850 C, its electrical resistance increased from 6 ohms to 9.1×10^4 ohms. During this time, the temperature of the capsule near the sapphire disc was about 5 C higher than that at the opposite reservoir-end.

Post examination of the sapphire-tantalum capsule revealed that it had lost all of its pre-charged potassium. The entire surface of the tantalum tube and the periphery of the sapphire disc was encrusted with a heavy white deposit. The density of a small sample of this white deposit was found to be 3.8 gm/cm^3 . The electrical resistance of the deposit sample, as measured with an electronic multimeter, was infinite at room temperature.

An attempt to charge the capsule made with a Lucalox tube and niobium end caps was unsuccessful. On removal of the charged unit from the glove box, the end cap with the filling tube was found to have cracked circumferentially at the stressed part of the niobium joint. The lower end of the capsule which remained intact was cut off, sealed in a stainless steel capsule and then exposed for 172 hours to potassium vapor at 850 C. The sample, identified as BK-26 in Table I, was unaffected by the exposure. The weight loss indicated for the sample may be due to oxidation of the niobium disc during the post exposure bake out.

3.3 Ceramic to Metal Seals - Fabrication

Four additional successful seals of sapphire to tantalum tubes have been made. These were similar to the two leak tight seals made previously, i.e., 1/2 inch O.D., 1/8 inch thick sapphire disc, with 30 mil tantalum wire in the center, brazed to a 1/2 inch O.D. tantalum tube with 95 Zr-5 Be alloy. The tube was flared out at one end to receive the sapphire disc. Tube length was 2 inches with a 30 mil tantalum wire serving as lead wire. All units developed leaks on prolonged thermal cycling. Cracks developed in the sapphire disc near the tantalum wire. This was probably due to differential thermal expansion.

Attempts at constructing Lucalox to tantalum tube seals with aluminum silicate glass was unsuccessful, due to cracking of the glass at the tantalum glass interface.

Attempts at constructing Lucalox to tantalum tube seals with 28.5% Ni-71.5% Ti were unsuccessful due to cracking of the brazing alloy at the seal. However, prospects for successful seals with this system seemed excellent in view of the last attempts, which indicated that lower processing temperatures (~ 1100 C) and thinner fillets result in crack-free seals with good bond strengths.

Lucalox to tantalum tube seals, using Mo-Mn-metallized

Lucalox discs in conjunction with Nicrobraz 130 alloy, were unsuccessful. Prospects for success here were poor as the Mo-Mn metallizing detached from the Lucalox when "wetted" with brazing alloy.

Techniques were investigated to join stainless steel tubes to the tantalum tubes to permit use of stainless steel Swagelok closures. One tantalum to stainless joint was made with Nicrobraz 130 in argon using a susceptor and induction heating. The other joint was made with Nicrobraz 130 in vacuum. In the assembly, a slip fit was made with the tantalum inside the stainless steel, the stainless walls were machined thin to permit movement without fracture.

Several attempts were made to metallize Lucalox with molybdenum-titanium so it could be brazed with the nickel base alloys. Fair coverage of the Lucalox with the Mo-Ti was obtained, but the Mo-Ti was partially dissolved by the nickel brazing alloy.

The 72% Ti-28% Ni alloy was also tested. It appeared to wet Lucalox and tantalum well. A sample exposed to potassium at 850 C parted at the interface (BK-15, Table 1).

A new approach was taken to combine a mechanical seal with a metallurgical bond. A shoulder was machined into a tantalum tube to provide a very close fit to a Lucalox

disc which was coated with Mo-5% Ti. The joint was heated to 1500 C for 20 minutes in argon, but the fitting was not good enough to establish a diffusion bond and the seal leaked. It was then brazed with a small amount of zirconium-5% beryllium. The projection of the tantalum tube above the Lucalox disc was thinned and spun onto the Lucalox. Tests are not complete on this specimen, but the Lucalox did not appear to crack. The results do indicate that a diffusion bond or a mechanical-metallurgical seal may be possible for the application. A combination of a mechanical seal and final braze with an active metal may provide a corrosion path long enough to do the required testing.

A high alumina-stainless steel seal was obtained from Auburn Spark Plug Co. This seal was welded to a one-inch stainless steel tube in preparation for testing in mercury vapor. After welding, the unit leaked (helium leak detector). A leak was detected between the alumina and the center lead. Attempts to seal this leak with glass caused complete failure.

3.4 Coating Methods

3.4.1 Vapor Deposition of AlN

An Oxalloy 28 wire coil which had been plasma sprayed with

alumina and then overcoated with vapor deposited aluminum nitride was exposed to potassium vapor at 850 C for 170 hours. During this treatment, much of the alumina chipped off. A disc of aluminum nitride, about 15 mils thick, which had been obtained by burning away its graphite substrate, was also exposed to potassium for 170 hours at 850 C with no degradation.

Coatings of AlN vapor deposited on Oxalloy wire always chip off upon cooling. X-ray diffraction analysis of the chipped material show that AlN is present. Also present is another material having an iron oxide pattern. Spectrographic analysis is being run on this material. Such an oxide could be present on the surface of the wire. This may be reacting with the vapors of the source material ($\text{AlCl}_3 \cdot \text{NH}_3$) to give the yellow film on the quartz tube, the presence of which was reported earlier.

Results of vapor deposition of AlN on nickel clad silver wire at 800 C were similar to those with the stainless steel clad copper wire. Even very thin coatings chipped off. The ends of the wire had been plated with about 7 mils of nickel to prevent the silver from vaporizing. This was effective for 2 hours at 850 C, but at 900 C, a mirror of silver was plated on the quartz reaction tube.

Thin films of aluminum nitride have been successfully applied to graphite, molybdenum and tungsten, but not to stainless steel, Inconel or nickel. It appears that the coefficient of thermal expansion of the substrate, as compared with that of aluminum nitride might be the controlling factor in the successful vapor deposition of aluminum nitride under these conditions.

Several attempts to apply aluminum nitride films to alumina or zirconia coatings which had been plasma sprayed onto nickel-clad silver wire were initially unsuccessful. The plasma sprayed coating chipped off upon cooling to room temperature from the aluminum nitride deposition temperature of 800 C. Some success was achieved with zirconia coatings which had an undercoat of nickel aluminide applied to the nickel-clad silver wire before spraying with zirconia. Aluminum nitride was successfully applied to a straight piece of wire which had been coated in this manner. It was also applied to three coils of wire which had been coated with zirconia in the same manner. The aluminum nitride partially chipped from two of these three coils.

The straight length of wire with the aluminum nitride overcoat on the plasma sprayed zirconia was exposed for 172 hours to potassium vapor at 850 C. Although pinholes in the end beads of the wire resulted in loss of the silver

core, the coating remained intact and a purple discoloration was the only change noted.

3.4.2 Plasma Sprayed Coatings

The sample of zirconia sprayed onto an Inconel substrate looked sufficiently good after exposure to potassium vapor at 850 C to warrant preparation of a wire coil. The conductor consisted of nickel clad silver wire preformed into the shape of the statorette coil. No difficulty was experienced in applying a uniform one mil coating.

The adherence of plasma sprayed coatings to nickel clad silver wire was not as good as to Inconel strip. Both substrates were sand blasted to promote adherence but the coatings cracked or came off the nickel clad silver when cycled to 850 C. The higher coefficient of expansion of the silver is undoubtedly the cause of the cracking.

Three inch long samples of nickel clad silver wire were plasma sprayed with alumina, magnesia and zirconia. These conductor samples had previously been nickel plated on the ends to prevent attack on the silver by the potassium. Two samples were prepared, one with the insulating coating completely covering the entire wire and the second with the insulating coating covering all but 1/4 inch at the

end. These samples were tested in potassium vapor to determine the adherence and resistance to potassium vapor at 850 C when coated on actual conductor materials.

The failure of the coated wire samples in potassium, as indicated in Table I, was attributed to adherence failure. The coatings which lifted were examined under a microscope and no attack on the coating themselves was noted. To alleviate this problem, all subsequent wire test specimens have been precoated with the Metco nickel aluminide alloy before application of the oxide coating.

Several specimens of the nickel clad silver wire were coated first with the nickel aluminide then zirconium oxide or aluminum oxide. These specimens were used as the base for application of aluminum nitride.

Samples of Inconel sprayed with magnesia and strontium zirconate were prepared. These two materials are not normally supplied in plasma spray grades. Optimum conditions for application were determined before making the test samples. The magnesia coated very well, but the strontium zirconate gave a rougher surface than desired. A change in mesh size of the latter material should alleviate the problem.

A new source of a plasma spraying grade of strontium zir-

conate, The Zirconium Corporation, was located and a trial lot of the material obtained. The material sprayed much better than the Titanium Alloy Mfg. Co's. (TAM) fine powdered strontium zirconate. The new material is also much purer than the TAM material. Direct spraying of the strontium zirconate onto an Inconel substrate did not provide sufficient adherence to pass the 850 C thermal cycle test. The use of nickel aluminide pre-coating again provided excellent adherence and specimens could be cycled to 850 C with no loss of adherence. This latter specimen was tested in potassium vapor.

Two coils were prepared and plasma sprayed with nickel aluminide followed by zirconium oxide. One of these coils was given an additional coat of aluminum oxide. These coils are expected to be resistant to potassium vapor.

3.4.3 Plasma-Arc Graded Coatings

Fifteen coils of the nickel clad silver wire, (No. 8 wire size), were preformed into a typical generator coil configuration. Four of these coils were then etched by a 1:1 chemical solution of 50% acetic acid - 50% concentrated nitric acid. This etched surface was then degreased with acetone before plasma-arc spraying. Molybdenum was sprayed on two of the coils over the nickel cladding. This molybdenum was plasma-arc sprayed using an argon plasma and

powder carrier gas. An inert argon atmosphere chamber was not used, however, no evidence of oxide could be found on the molybdenum surface.

Nickel aluminide was also plasma-arc sprayed on nickel clad silver coils. This created a surface to which the zirconia, alumina would adhere. The compositions of these insulated conductors are as follows:

1. A two mil coating of molybdenum followed by a three mil coating of 99% alumina.
2. A two mil coating of molybdenum, two mil coating of alumina and finally a two mil coating of zirconia.
3. A two mil coating of nickel aluminide, two mil coating of 99% zirconia (Hafnia free). The final coat was two mils of alumina (99%).
4. A two mil coating of molybdenum, two mil coating of zirconia, followed by a two mil coating of alumina (99%).

Figure 9 shows examples of coated and uncoated nickel clad silver conductors.

3.4.4 Materials Analysis

In order to interpret the results of the potassium environ-

mental tests on various insulators, it was necessary to know the impurity content of the materials used. Table 3 has been compiled to show the chemical analysis of some of the materials tested. An analysis on all materials was not readily available from the suppliers. On those materials that failed to pass the potassium environmental tests, the chemical analysis will not be obtained.

3.5 Adherence Testing - Ceramic Insulation

Samples of two ceramic insulated nickel clad silver wire coils were subjected to vibration, shock, and acceleration. The description of their fabrication is as follows:

1. A preformed coil of (23%) nickel clad silver wire No. 8 (.128" O.D.), plasma-arc sprayed with nickel aluminide, zirconia (99%) and alumina (98%).
2. A preformed coil of (23%) nickel clad silver wire, No. 8 wire size, plasma-arc sprayed with molybdenum, zirconia and alumina.

One inch pieces of the insulated wire described as No. 1 were used to space and securely wedge a coil of No. 2 (preceding description) into a statorette made of 4 mil Hiperco punchings. This assembly was then bolted to a

test fixture. Figure 10 shows the statorette test assembly. The following test conditions were imposed on this assembly.

3.5.1 Vibration

The statorette was subjected to cycling vibration from 80 to 2000 cycles with an input acceleration of 20 g. The rate of change was logarithmic and such that one hour was required to proceed from 80 to 2000 and back to 80 C.P.S. The cycling test period for each of the mutually perpendicular axis was two hours, making a total test time of six hours. This testing was conducted at a laboratory ambient temperature of $\approx 23^{\circ}\text{C}$.

3.5.2 Shock

A mechanical shock of 50 g was applied to the statorette in each direction of the three mutually perpendicular axis three times for a total of 18 impact shocks. The machine used was a Machine Dynamics Inc., Model DS9-4.

3.5.3 Acceleration

The acceleration testing was conducted on the statorette assembly in accordance with Procedure 1, Mil-E-5272C.

The electrical leakage at 500 volts 60 cycles of 2.8 micro-

amperes was determined before the adherence tests and did not change after vibration, acceleration, and shock testing.

3.6 Humidity Testing

A nickel clad silver wire coil coated with molybdenum, zirconia and alumina was exposed to 100% R.H. for ten days. An electrical leakage determination on this coil before exposure was 2.8 micro-amperes at 500 volts, 60 cycles. One hour after completion of exposure to humidity for ten days, the leakage was 96 micro-amperes at 500 volts.

3.7 Future Work

Selected ceramic insulated clad silver coils will be subjected to 850 C potassium vapor exposure for 3000 hours or until failure of the insulation in a statorette.

Typical insulation combinations are as follows:

- 3.7.1 Nickel clad or Inconel clad silver wire No. 8 size overcoated with plasma-arc sprayed molybdenum followed by zirconia, alumina.
- 3.7.2 Nickel clad or Inconel clad silver wire coated with nickel aluminide, zirconia, alumina coatings.
- 3.7.3 Nickel clad or Inconel clad silver wire coated

with molybdenum, followed by strontium zirconate.

3.7.4 Nickel clad or Inconel clad silver wire coated with nickel-aluminide, strontium zirconate combination.

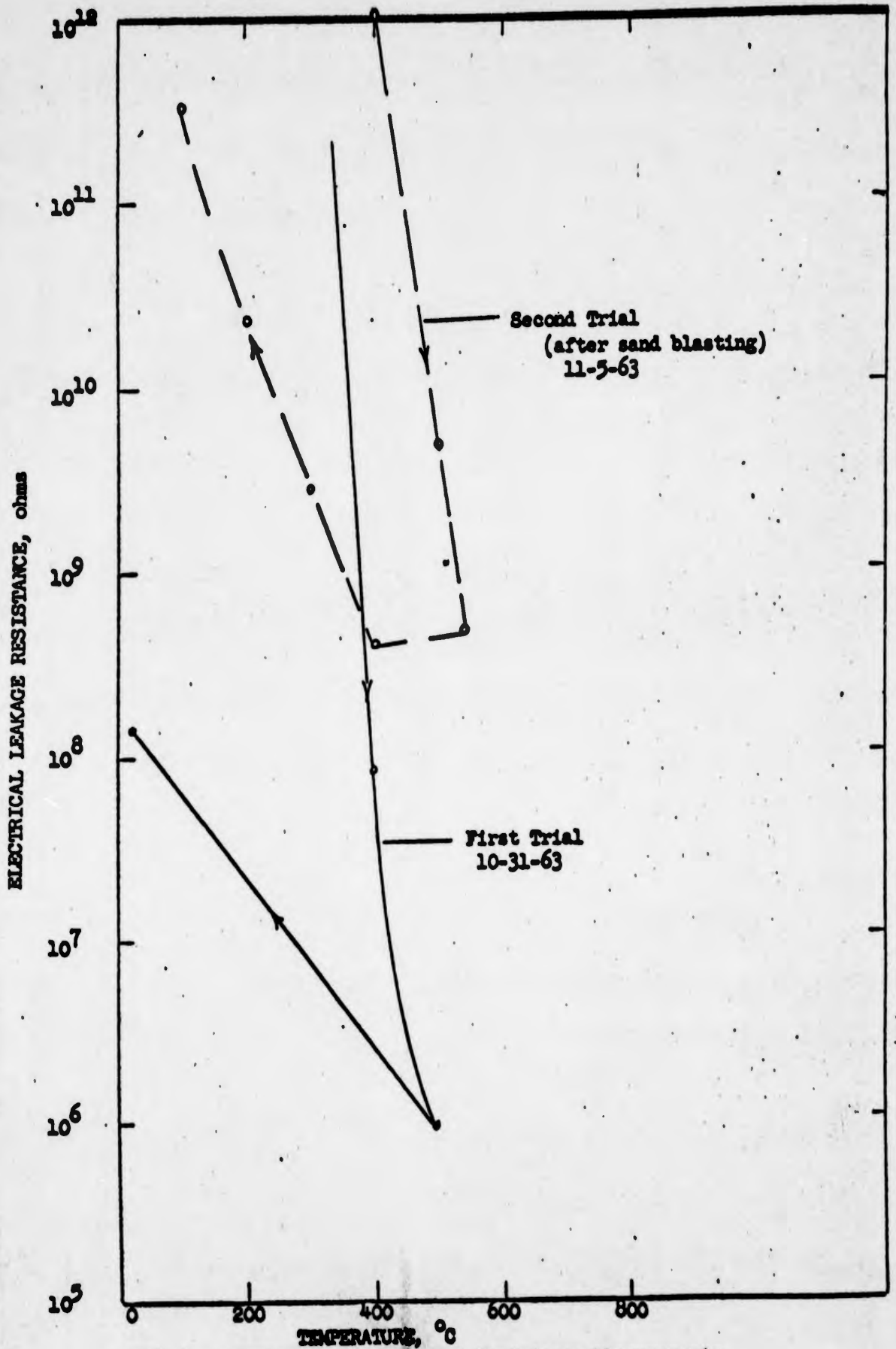


FIG. 1 -- Temperature-Electrical Resistance Measurements of a Tantalum-LiicaloxSeal in Argon.

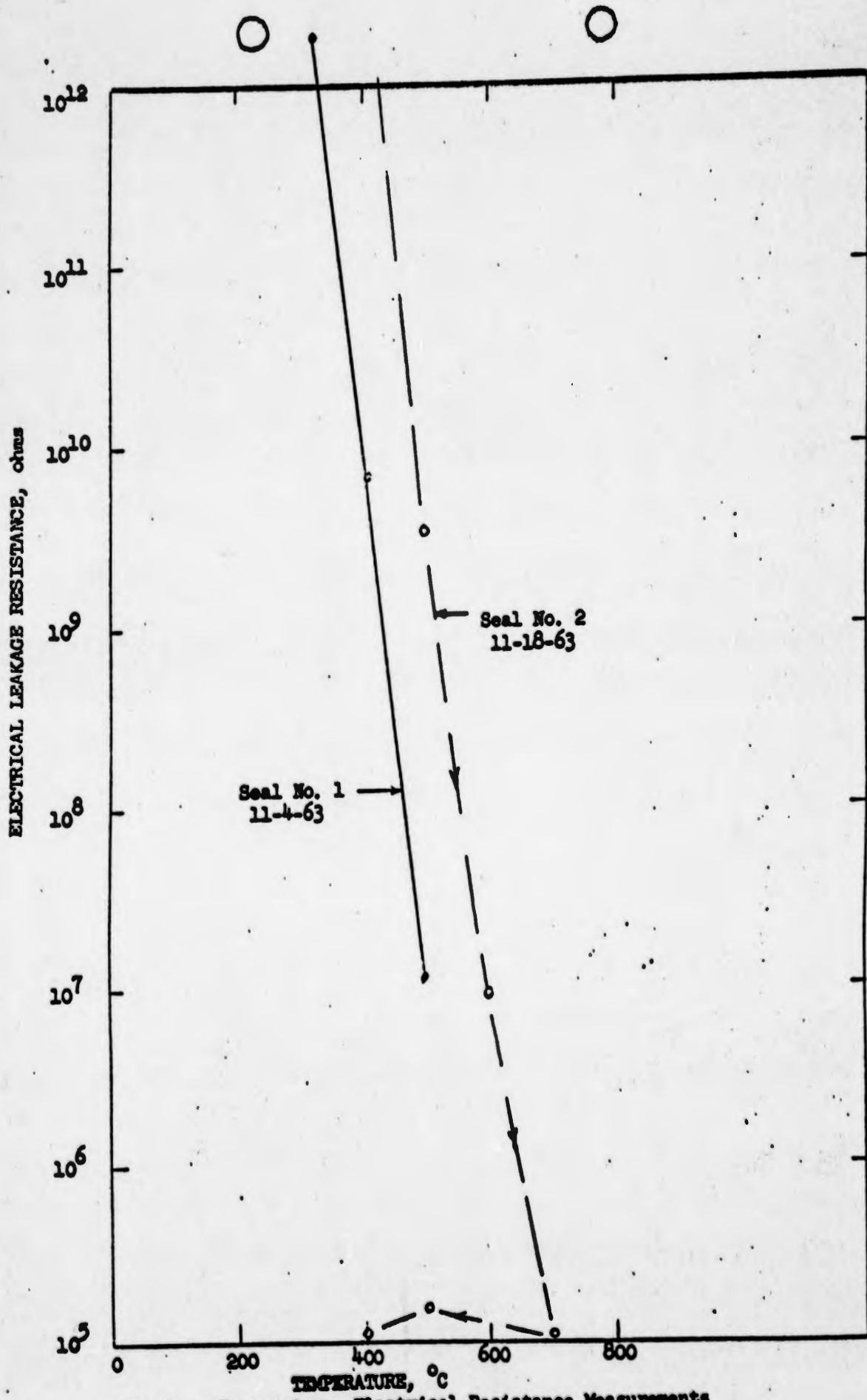


FIG. 2 -- Temperature--Electrical Resistance Measurements of Tantalum-Sapphire Seals in Argon

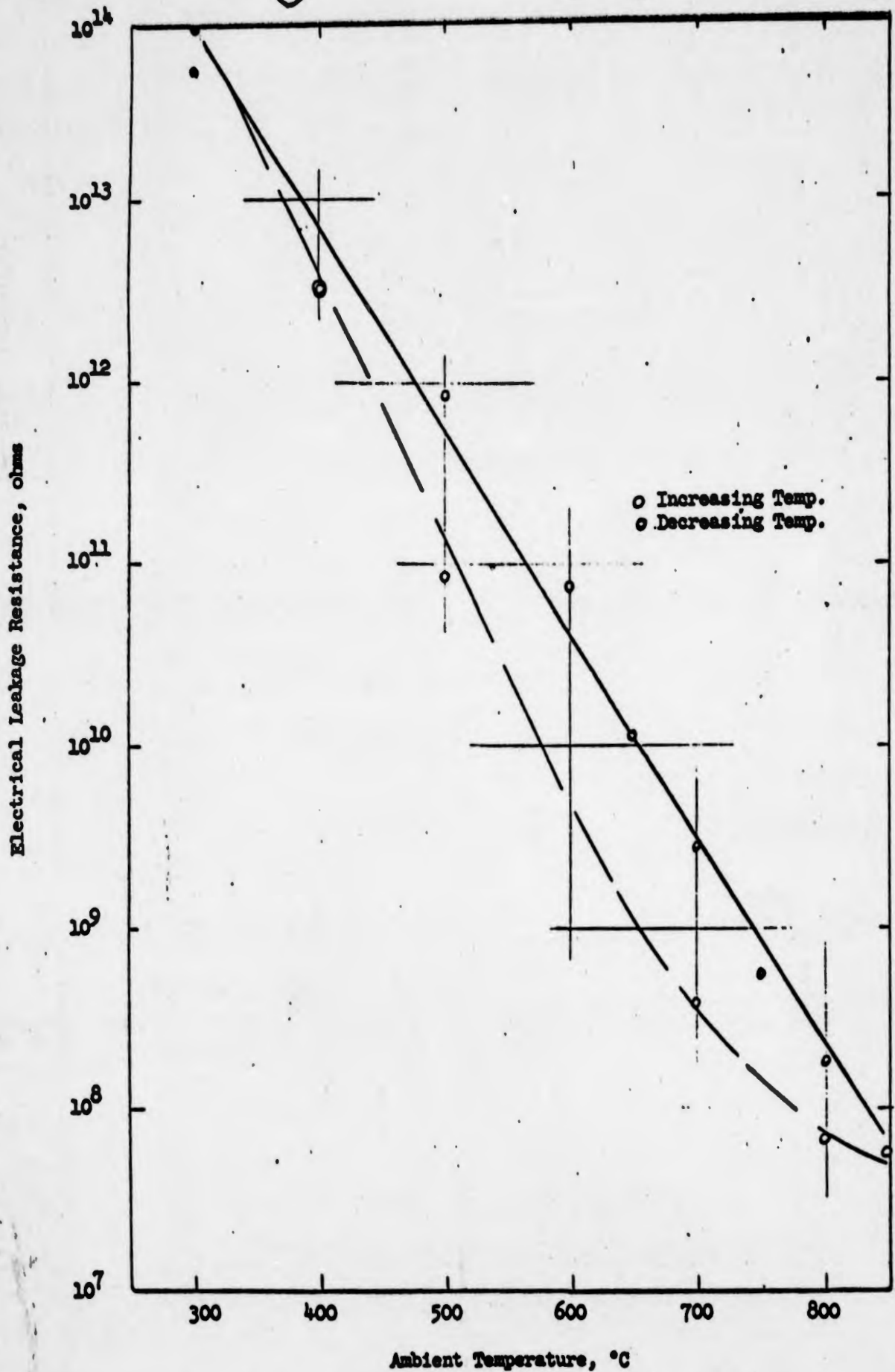


Fig. 3 - Tantalum-Sapphire-Tantalum Seal (Uncharged) in Argon.

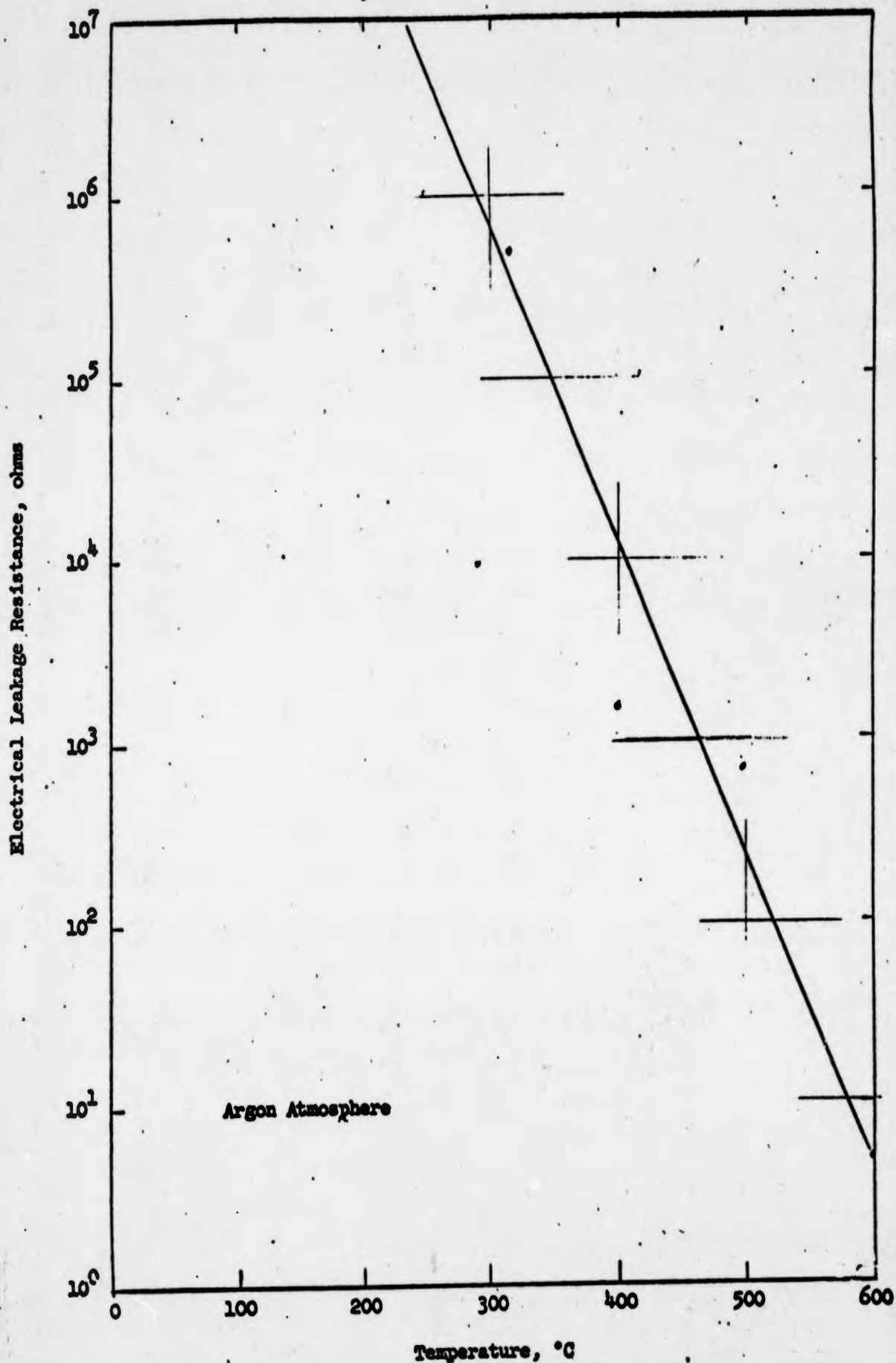


Fig. 4 - Electrical Leakage Resistance of Flame Sprayed Zirconia on a 1/8" dia. Nickel Rod. (12 mil total build)

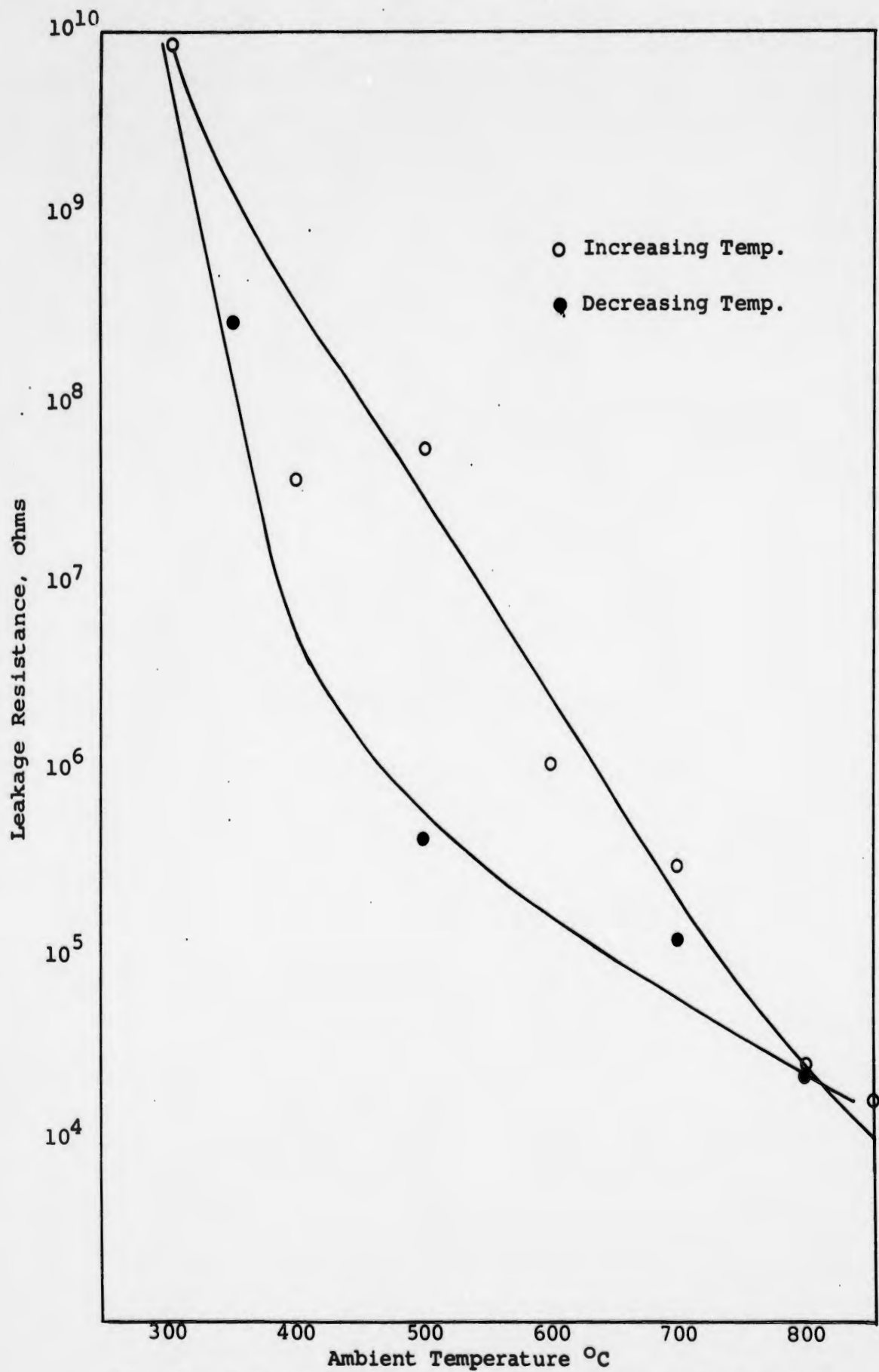


Fig. 5 - Leakage Resistance vs Temperature-Coil of Nickel Clad Silver Wire, 1-2 mils NiAl (Basecoat), 1-2 mils ZrO₂, AlN (Overcoat)

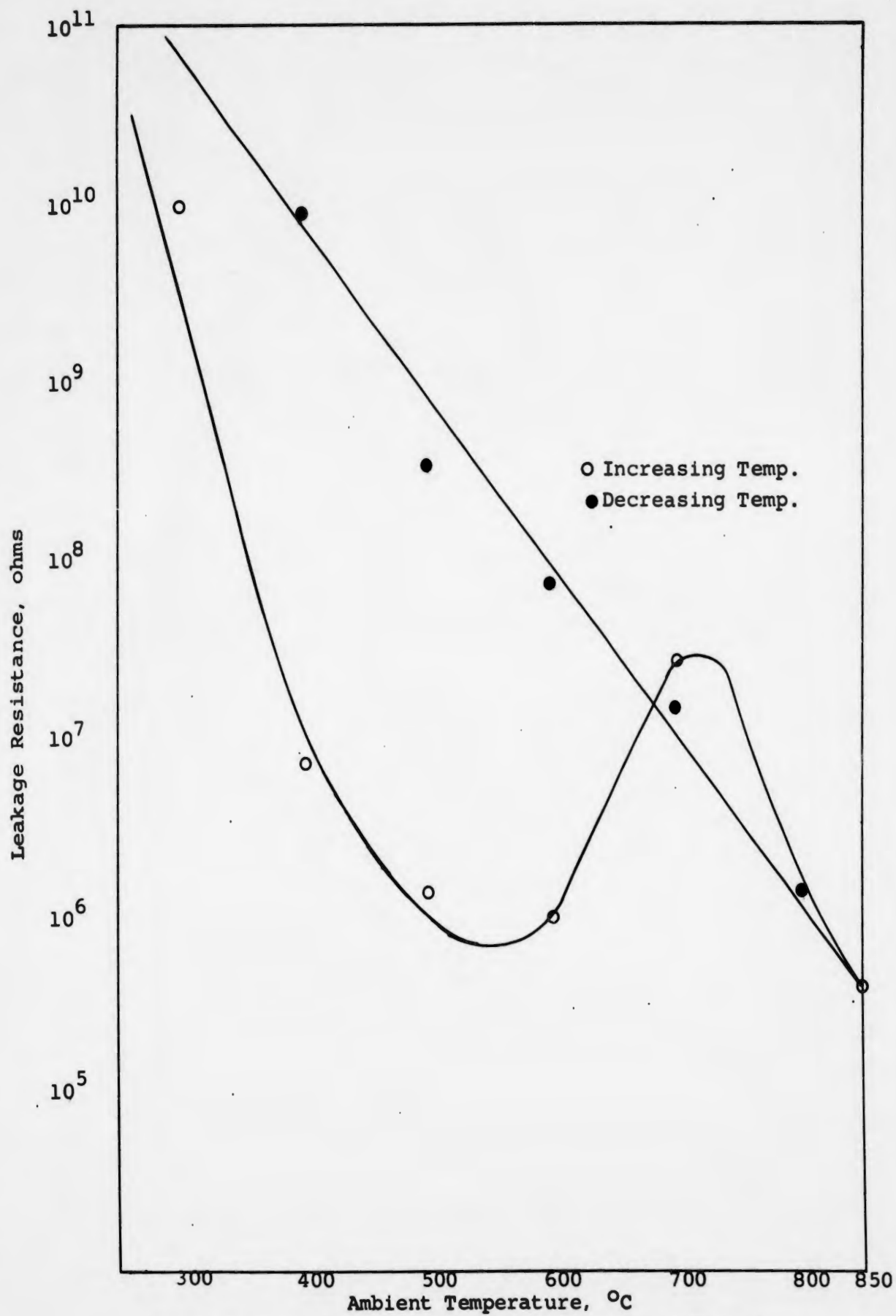


Fig.6- Leakage Resistance vs Temperature - 1/8 inch Molybdenum Rod Coated With AlN

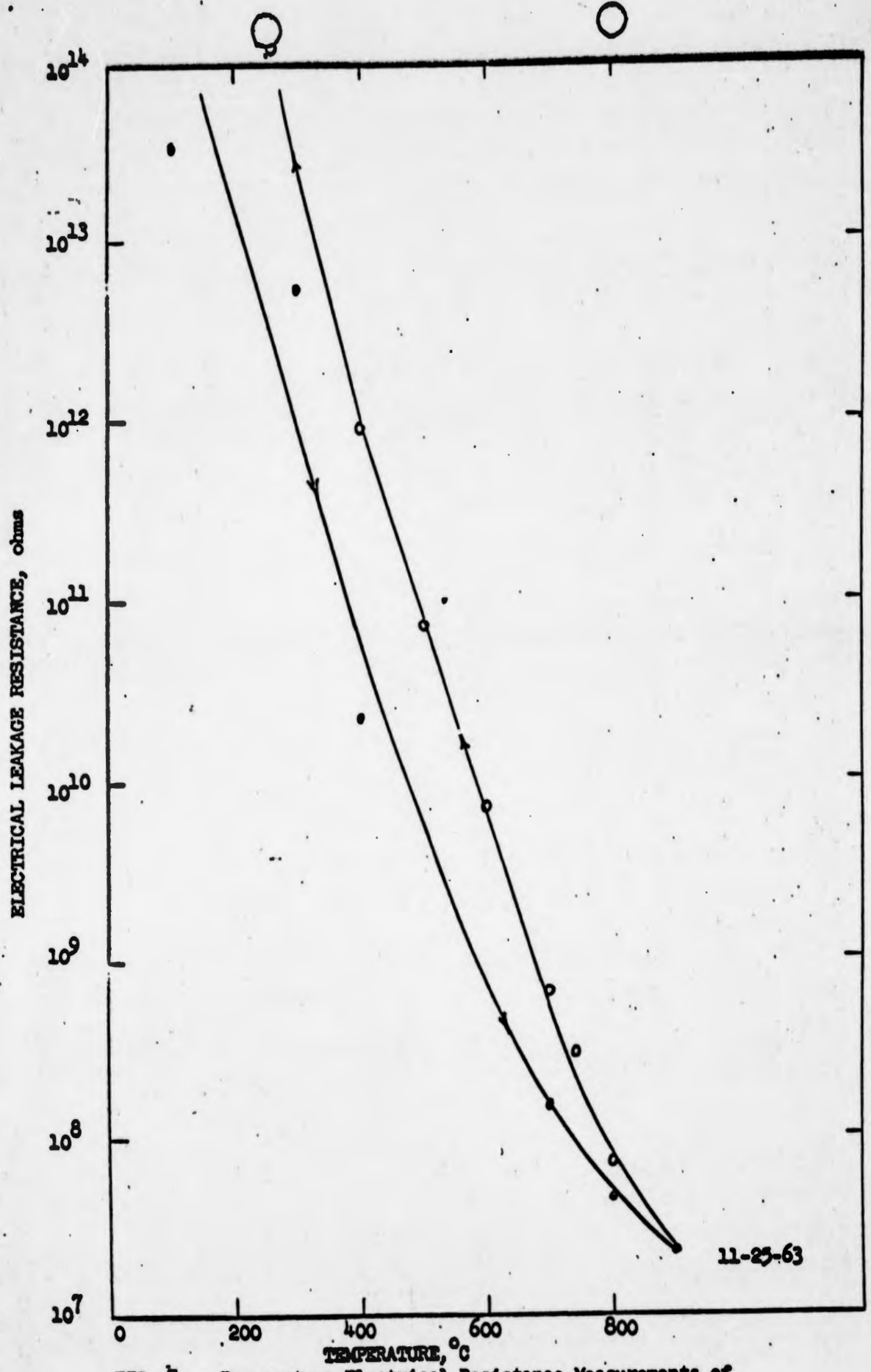


FIG. 7 -- Temperature-Electrical Resistance Measurements of an Alumina-Niobium Seal in Argon.

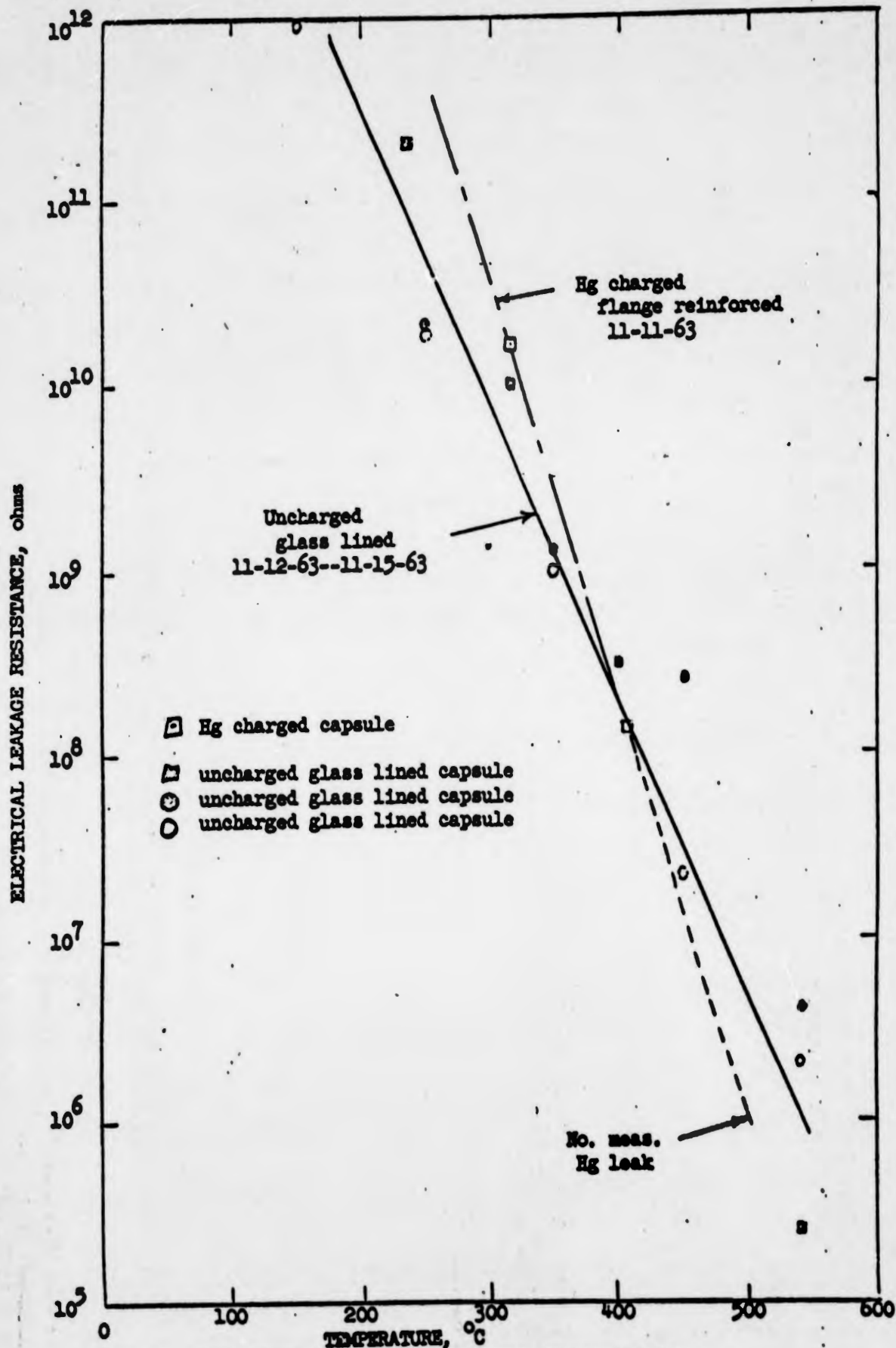
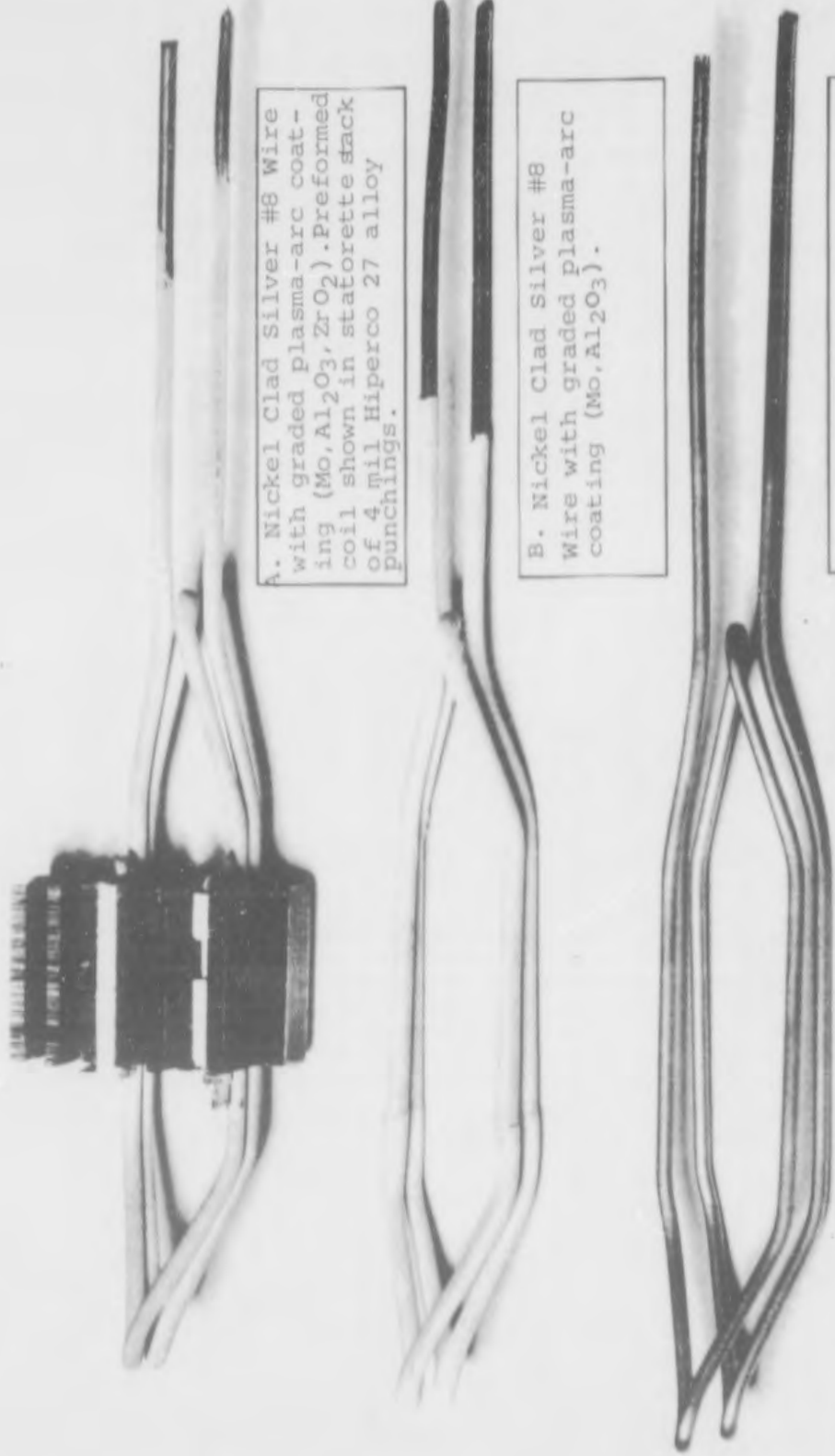


FIG. 8--Temperature-Electrical Resistance Measurements of Alite C-500 Terminals



A. Nickel Clad Silver #8 Wire with graded plasma-arc coating (Mo, Al₂O₃, ZrO₂). Preformed coil shown in statorette stack of 4 mil Hiperco 27 alloy punchings.

B. Nickel Clad Silver #8 Wire with graded plasma-arc coating (Mo, Al₂O₃).

C. Nickel Clad Silver #8 Wire chemically etched - uncoated.

Figure 9 Preformed Nickel Clad Silver coils with and without ceramic insulation.

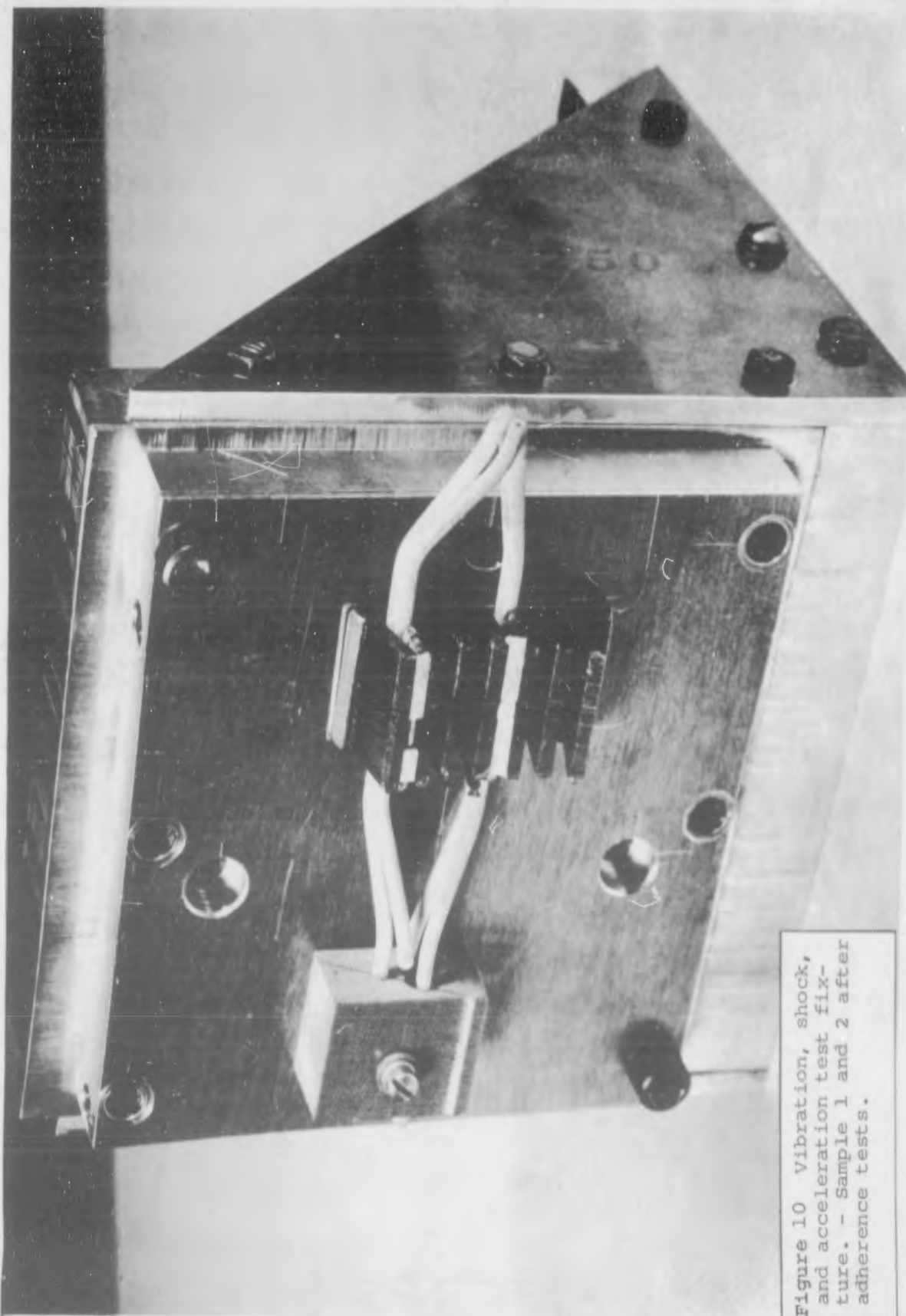


Figure 10 Vibration, shock, and acceleration test fixture. - Sample 1 and 2 after adherence tests.

TABLE 1

POTASSIUM VAPOR EXPOSURES AT 850 C - 170 HOURS

WEIGHT INFORMATION

IDENTITY	SAMPLE	BEFORE	AFTER	CHANGE	COMMENTS
BK-9	Microbraz 130-Vac. Heated	1.1684	1.1678	-.0006	Some discoloration.
BK-10	Microbraz 130-Argon Heated	.9790	.9789	-.0001	Some discoloration.
BK-11	28 Ni-72 Ti	.6326	.6289	-.0037	Some discoloration.
BK-12	62.5 Ti-37.5 Ni	.4429	.4488	+.0059	Sample darkened appreciably.
BK-13	Lucalox/Ta joint-72Ti/28Ni	.3299	.3280	-.0019	No apparent change.
BK-14	Lucalox/Ta joint-72Ti/28Ni	.8928	.8884	-.0037	Sample broke apart.
WK-11	Ni clad ag-ends electroplated with Ni	6.9429	6.9334	-.0095	No apparent change.
TK-12	Plasma sprayed MgO on Ni	11.7598	11.7488	-.0110	Sample intact, coating has soft appearance.
CK-30	Alite, A-610 insulator				
CK-27	99 Al ₂ O ₃ - 1 MgO ALN film	2.1235 0.0779	2.1235 .0635	0 .0144	Sample darkened to light grey. No apparent change, sample chipped.
CK-28	ALN coated graphite	2.4578	--	--	Graphite disintegrated.
CK-29	Al ₂ O ₃ /ALN on St.St. clad Cu	4.1414	3.6396	-.5018	Coating lifted from wire.
WK-12	Metco 115 ZrO on Ni Clad Ag wire	4.4192	--	--	Film lifted.
WK-13	Metco 105 Alumina on Ni clad Ag wire	4.9675	--	--	Film lifted.
WK-14	Metco 201 ZrO on Ni clad Ag wire	4.6750	--	--	Portions of film lifted*.
WK-15	Same as WK-12 except wire ends not coated.	4.5690	--	--	Film lifted.
WK-16	Same as WK-13 except wire ends not coated.	4.7636	--	--	Film lifted.
WK-17	Same as WK-14 except wire ends not coated.	4.6193	--	--	Portions of film lifted*.
WK-18	ALN overcoat-Metco 201 ZrO on NiAl coated Ni clad Ag wire.	5.2995	**	--	Coating intact with purple discoloration.
WK-19	Alumina on Mo coated Ni clad Ag	6.5888	--	--	Coating cracked and lifted.

* Specimen may have been damaged during removal from capsule.

** Silver core lost due to pinholes in beads sealing wire ends, therefore, weight change data not significant.

TABLE 1 (Cont 'd)

POTASSIUM VAPOR EXPOSURES AT 850 C - 170 HOURS

IDENTITY	SAMPLE	WEIGHT INFORMATION			COMMENTS
		BEFORE	AFTER	CHANGE	
WK-21	Metco 1115 ZrO on Ni rod.	4.7724	4.6854	-.0870	Coating lifted and cracked.
WK-22	Metco 201 ZrO on Ni rod.	4.6831	4.5987	-.0844	Coating lifted (Capsule leaked).
WK-23	Metco 201 ZrO on NiAl (Metco 404) coated Ni rod.	4.8358	4.8349	-.0009	Slight purple discoloration, (no peeling apparent).
CK-30	Norton-Magnesia on metal bar.	14.0136	14.0445	+.0309	Capsule leaked.
CK-31	Strontium Zirconate on metal bar.	14.7999	14.8700	+.0701	Capsule leaked.
CK-32	Hot pressed AlN (Cerac 4)	.6735	.6638	-.0097	No apparent change.
WK-24	Same as WK-21 except rod ends uncoated.	4.8950	4.8336	-.0614	Coating lifted.
WK-25	Same as WK-22 except rod ends uncoated.	3.6708	3.6439	-.0269	Coating lifted-(Capsule leaked).
BK-26	Lucalox/Nb joint using alumina-calcia glass.	5.5246	5.5030	-.0216	No apparent change.***
	Strontium zirconate over NiAl coated Inconel strip.	14.3980	--	--	Coating lifted as one piece at NiAl interface.
	Metallized A610 OFHC Cu brazed to A nickel and Ni plated	4.1415	--	--	Sample broke apart-heavy attack on A610 body at brazing interface.
	Lucalox disc TiNi brazed in Ta tube	3.2127	2.9719	-0.2408	Purple deposit on Lucalox unit not leak tight after exposure.

*** Post exposure bake out of specimen resulted in some oxidation of niobium cap.

TABLE 2

Mercury Exposure Tests at 540°C - 100 hours

<u>Identity</u>	<u>Sample</u>	<u>Wt. Info.</u>			<u>Comments</u>
		<u>Before</u>	<u>After</u>	<u>Change</u>	
BH-6	63 Ti-27 Fe-10 V	.5452	.5454	+ .0002	No apparent change.
BH-8	68 Ti-28 V-4 Be	.1118	.1104	- .0014	No apparent change.
BH-12	62.5 Ti-37.5 Ni	.1303	.1303	--	No apparent change.
BH-13	Ta/Lucalox with 62.5 Ti/37.5 Ni	.8486	.8489	+ .0003	No apparent change.
BH-14	95 Zr-5 Be	.0846	.0703	- .0143	Darkened by HNO ₃ dip.
BH-15	71.5 Ti-28.5 Ni	.1327	.1300	- .0027	No apparent change.

TABLE 3

Purity of Various Insulators Tested for Potassium Resistance

Weight Percent of Impurities

Material	Al ₂ O ₃	MgO	ThO ₂	ZrO ₂	CaO	BeO	SiO ₂	TiO ₂	Fe ₂ O ₃	Nw ₂ O	SrO	BaO	BN	Unknown
Alumina AD99	99.0						3*	2.3*	2*					1.0
Metco 101	91+						2*							1.0*
Metco 105	96+													1.0*
Lucalox	99.9	0.1												
Sapphire	100.0													
Zirconia														
ZrO-CaO	0.18	0.25		93.5	4.80		0.62	0.11	0.10					0.65
Metco 201	0.5			93.5	5.0		0.35							
Thoria			99.5+											0.5*
Beryllia						99.5								0.5
Magnesia														
Single Crystal	.02	99.5+					0.08		0.05					
Flame Spray	0.26	96.4					1.21		.23					
Strontium Zirconate														
Y-628	0.07	0.24		53.9			0.24	0.07						
Y-760	0.07	0.24		53.9			0.24	0.07			45.3			
Flame Spray - TAM	0.31	0.05		51.0	0.15		3.75	0.34	0.16		45.3	0.80		
BN	0.20*	0.10					0.20*						99.5	
Wire Coating 15A7SS														
Alumina	99.65	0.08		0.08	0.08		0.08		0.10	0.06				
Colloidal ZrO ₂	96+						.04		.12					

*Maximum

+Minimum

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