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

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DEVELOPMENT OF HIGH TEMPERATURE ALKALI METAL RESISTANT INSULATED WIRE

2nd Quarterly Progress Report
Contract AF33(657)10701, Task No. 8128-08

August 15, 1963

Westinghouse Electric Corporation
Aerospace Electrical Division
Lima, Ohio

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.

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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 second 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. Some forty-seven exposure tests were initiated during the period and the test results indicated high purity alumina, magnesia, boron nitride, aluminum nitride and beryllia as well as Oxalloy 28, a stainless steel clad copper core conductor, were resistant to both environments. The fusion coating technique is the only coating process by which coated wire samples for metal vapor corrosion testing have been produced to date. In the initial screening tests, one potting compound, containing zirconia and alumina, was promising enough to merit further testing. Initial test results from trials to densify porous coatings by mass transport of material were very promising. Difficulty in fabricating a seal between the lead-in insulator and the electrical test capsule prevented initiation of electrical tests on the materials in the metal vapor environment.

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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. Twenty-three mercury (538°C) vapor and twenty-four potassium (850°C) vapor exposure tests were initiated during this quarter. The test results indicate high purity alumina, magnesia, beryllia, boron nitride and aluminum nitride exhibit good resistance to potassium vapor. Pyroceram, Sauereisen #8 and boron phosphate showed the least resistance to potassium vapor. All insulators had good resistance to mercury vapor.

2. Metallurgical examination of conductor samples exposed to metal vapors showed no significant attack on the Oxalloy 28 wire by either the potassium (172 hours at 850°C) or the mercury (340 hours at 538°C) vapors. No grain growth was evident in the copper core. Both the nickel plated and nickel clad wires evidenced severe attack and measurable grain growth of the copper core.

3. Silica modified alumina and alumina-magnesia slurries were dip coated on Oxalloy 28 wire and fired at 1000°C to produce uniform, adherent insulating coatings. The coating breakdown strength ranged from 250 to 650 volts.

4. Nine potting compounds were screened. One new formulation containing alumina and zirconia, exhibited high enough strength after firing to merit further evaluation.

5. Initial results from attempts to densify porous coatings by mass transport of material from the outer coating to the conductor-coating interface were very promising. About 0.1 gram of alumina was transported a distance of 15 cm in a dry HCl (10 atm.) atmosphere across a thermal gradient.

6. The resistance of Oxalloy 28 wire was measured during a 500 hour aging run in argon at 540°C. The resistance values measured during heat-up, aging, and cool-down never exceeded 131% of that of the copper standard at the same temperatures.

7. A test circuit was designed and built, which measures with minimum error, the resistance of insulators at temperatures up to 850°C. Measurements on a sapphire (Linde Co.) specimen showed a resistance decrease from 8×10^{12} ohms to 1.9×10^{8} ohms during heat-up from 350°C to 850°C.

8. Attempts to form a stable boron nitride coating by decomposition of "B" trichloroborazole have been unsuccessful to date. Adherent, glossy insulating films have been formed on a variety of metal substrates but the films flake off when exposed to air for a short time. Adherent, insulating films have not been successfully formed in Inconel surfaces.

9. Attempts to form zirconia and alumina coatings by evaporation of the pure metals in a reduced (10^{-3} torr) atmosphere of oxygen (flowing)

were not successful. No measurable coatings of zirconia were deposited and the alumina coatings formed contained some aluminum metal in the layers. No further work is presently planned on this technique.

10. Attempts to form an alumina coating on a metal substrate by thermal decomposition of aluminum isopropoxide were unsuccessful. The coating formed preferentially on carbon deposits in the reaction vessel. Additional trials will be made using other materials such as aluminum methoxide and aluminum chloride.

11. Additional plasma spray equipment was installed during the quarter because the work load on the existing equipment prevented any extensive investigation of this coating technique.

12. Data was obtained from the literature on breakdown voltages of potassium and mercury vapor.

13. Equipment was set up to attempt formation of an aluminum trifluoride coating. The outer surfaces of the coating will be converted into an aluminum nitride or alumina sheath to provide the necessary resistance to metal vapor attack.

14. The lead-in insulator to electrical test capsule seal continues to present problems. Conventional brazing alloys such as the Nicrobraze alloys did not wet unmetalized, high purity ceramics. Trials

with exotic alloys such as Zr-Ti-Be have been planned. Successful alumina to alumina, and alumina to niobium joints have been made by means of a calcia-alumina mixture and a modified aluminum-magnesium-silicate.

III. FUNDAMENTAL CONSIDERATIONS OF CORROSION RESISTANCE

3.1 Insulators

3.1.1 Kinetic Processes

The processes involved in the destruction of a material by liquid metal vapors are primarily solvent attack, corrosion or both. In general, both of these processes increase in severity with increasing temperature and at a rate dependent on the type of liquid metal and the material being attacked.

The depth of diffusion of a metal vapor into a solid is a function of time. The crystalline structure, porosity, products formed, pressure and temperature determine the rate of diffusion. Since the depth of diffusion[1] is a fractional power of the rate times the time $\sqrt[x]{(\text{rate})(\text{time})}$ the process has a tendency to be self limiting.

Diffusion rates for metal vapor are important in this study in two cases, 1) when the insulating material is unaffected and 2) when any reaction product is not removed from the surface. On the other hand, when a reaction product forms and is removed by excess metal vapor, the rate of attack is otherwise controlled. Since the former are most important for metal vapor resistant insulation, low diffusion rates are necessary to maintain good insulation resistance on the surface of the insulator.

3.1.2 Microstructure, Microfissures, Phase Composition

In considering insulating materials, the ideal structures for optimum corrosion resistance are single crystal inorganic compounds. A number of materials are available as single crystals, but formation of single crystals on conductors is very difficult. Polycrystalline compounds are more easily obtainable and applied, but unless they are near theoretical density, they allow metal vapors to penetrate into the surface. Since single crystal and dense polycrystalline materials are relatively inflexible, they crack off or develop microfissures on bending, allowing penetration of the metal vapors. When crystalline materials are applied to substrates, microfissures can also develop during thermal cycling due to excessive stresses, resulting from unequal coefficients of thermal expansion of the two materials.

The different phases of pure oxide materials probably show little variation in their corrosion resistance. However, the small amount of impurities that are necessary for the formation of certain phases could grossly affect corrosion resistance, depending on the compound present.

3.2 Materials Selection Based on Theoretical Considerations

3.2.1 Non-Conductors

The materials selected based on theoretical considerations were

single crystal and polycrystalline pure oxides. The limited data available on resistance of oxides to metal vapors indicated pure oxides resist metal vapor attack better than multiple oxide crystalline materials or glasses.

When considering various oxide materials for resistance to metal vapors in electrical devices, their conductivity becomes important. An oxide which is resistant to metal vapor must also be an electrical insulator at the operating temperature. Thus a large number of potential materials are eliminated, at least initially, because they have less than one megohm insulation resistance at either 540°C or 850°C. In general, single crystals of an oxide are better insulators than polycrystalline forms. This is due to less ionic conduction and a lower impurity content in crystals. A multiple oxide compound is not as good an insulator as the best single oxide insulator in the compound. In considering any material from single crystals to commercial multiple oxide ceramics, the insulation resistance can vary considerably due to the amount and type of impurity in the structure.

Insulating coatings for conductors should ideally be thin continuous single crystals which exactly match the coefficient of thermal expansion of the conductors. Since metal vapor resistance, insulation resistance and conductor conductivity limits the availability of usable oxides and conductors, ideal condi-

tions do not prevail. The materials considered for the insulating coatings are the pure oxides previously mentioned. In addition, certain nitrides appear promising as insulators.

3.2.2 Conductors

The approach taken with respect to the electrical conductor was to use the best available conductor rather than try to develop a special one. Data from other work, such as that of Anaconda on AF33(616)7473, indicated conductors were available for the temperatures being considered, but their compatibility with the metal vapors had to be determined. The conductivity and other requirements limit the conductor choice to either copper or silver.

When considering the metal vapor corrosion resistance of silver and copper conductors, the deteriorative effect of mercury and potassium vapors necessitates a clad conductor. The problem then resolves into a suitable cladding material which shows no destructive grain growth and low diffusion rates between the conductor and cladding. Sufficient data is available on the liquid metal resistance of metals[2] to select candidate cladding materials with some assurance of good performance.

Grain growth must be considered in copper core conductors because excessive grain growth could rupture the cladding or dislodge the insulating material on the surface. The low

diffusion rate of metal between the conductor and cladding, although not a problem of corrosion, is important to maintain high conductivity in the conductor.

3.2.3 Coating Processes

In evaluating methods of coating conductors, the temperature limitation on the conductor has eliminated fusion coating with single pure oxides. Therefore, the coating processes under investigation are directed towards forming thin polycrystalline coatings at temperatures of 1000°C or less. One fundamental requirement of all these processes is that a dense, pore-free coating must be formed to resist penetration of metal vapors. Another requirement is to obtain a uniform coating on all sides of the conductor by a non-shadowing process. Since a flexible coating is not expected, the coating processes must be adaptable to preformed configurations.

3.2.4 Hermetic Seals

The corrosion problems associated with the hermetic seals necessary for electrical testing of insulators in metal vapor environments are basically the same as those discussed for conductors and insulators.

The metal conductor and the insulating portion must be resistant to metal vapors. In addition to this, the bonding material between the metal and insulator must be considered. Many of the

more common metalizing materials and glassy type bonding materials cannot be considered because of their known poor resistance to liquid metal vapors.

IV. EXPERIMENTAL WORK AND EVALUATION OF RESULTS

4.1 Metal Vapor Exposure, Mercury and Potassium

4.1.1 Test Capsules, Design and Fabrication

Figure 1 contains a detailed drawing of the corrosion test capsules and a flow diagram illustrating the techniques used to clean and fabricate them. The I.D. of the capsules for the third quarter work are being increased to 5/8 inch to accommodate larger test specimens, such as the 1/2 inch diameter metal to ceramic seal specimens.

4.1.2 Exposure Test Samples

During the second quarter, seventeen ceramic specimens were exposed to mercury vapor at 538 C and twenty-one to potassium vapor at 850 C. In addition, six copper core wire samples containing various cladings or plated coatings were exposed to the mercury environment. Three of these wire specimens were also exposed to potassium vapor. The materials tested are listed in Tables I and II.

The specimens are tested in the as received condition, except for the conductor specimens where the ends were welded to prevent attack on the cores. The insulator specimens were of varied shapes and sizes since most of the candidate materials are only available in specific forms.

4.1.3 Loading, Sealing and Leak Testing

The flow diagram in Figure 1 also illustrates the technique used to fill and seal the capsule. Capsule sealing techniques have proven acceptable by the successful completion of preliminary exposure tests in mercury for 340 hours and potassium for 172 hours without leakage.

The test capsules were loaded in a large glove box capable of evacuation to 1 x 10^{-3} torr. The box was evacuated and pressurized with purified argon several times prior to opening the containers of purified liquid metal. Capsule charging was carried out in the purified argon gas environment following the procedure illustrated in Figure 1. The loosely capped tube was easily evacuated when the dry box was evacuated to 1 x 10^{-3} torr. The Swagelok fitting was then remotely tightened by means of an electric wrench.

Argon cover gas was purified in a bubbler using NaK 78 at 600 F to reduce the O_2, N_2 and H_2O content to about one ppm. The potassium used in the preliminary tests was obtained from MSA Research Corp. and has an oxide content of 100 ppm. Oxide content of the potassium can be determined, when necessary, by the mercury amalgamation technique described by Champiex, et al[3]. The mercury metal as obtained from the supplier had about 5 ppm contaminate.

Loaded capsules were placed in Lindburgh furnaces. The potassium vapor samples were aged at 850 C and the mercury vapor samples were aged at 538 C. The temperature in the furnaces was controlled within ±4 C. Capsule arrangement in the furnaces is such that none of them can shield any other from the heater bars.

In view of recent difficulties experienced with the electric wrench (components arcing to ground), various rotary seal designs are being considered for the glove box that will permit the manual tightening of the Swagelok cap. The use of a manual technique would eliminate a problem currently existing that requires periodic rebuilding of the wrench motor windings. There is a good possibility that this modification in the sealing technique will be incorporated next month.

4.1.4 Sample Removal and Preparation for Examination

Samples were removed from capsules under argon while the potassium was in a molten state. This was necessary since in many cases the sample was coated with potassium and adhered to the support when the potassium became solid. After removal from the capsule, the samples were placed in a screw cap bottle and allowed to cool. The samples were then removed from the dry box after filling the bottle with isobutanol. When gas evolution stopped, or after 15 hours, (whichever was

longer) the samples were washed first in methyl alcohol and finally in water. Following the water wash, the samples were rinsed in methyl alcohol and placed in a quartz tube which was then evacuated to 1 micron. After reaching the desired pressure, the quartz tube was heated to near red heat for 5 minutes and the samples allowed to cool under the reduced pressure for one hour. Weight determinations were made immediately following this treatment.

The cleaning procedure for preparing specimens for examination after exposure to mercury has recently been changed. Rather than subject the sample to a dilute nitric acid dip, it has been decided to heat the samples to 350 C at a pressure of 1 torr to evaporate the mercury from the sample surfaces. This technique eliminates the possibility of forming a nitrate on the sample surfaces. The eleven tests listed in Table I as not completed will be cleaned in this way.

4.1.5 Evaluation of Corrosion Effects

4.1.5.1 General Observations and Weight Changes

The results of the exposure tests conducted during this quarter are given in Tables I and II. In those cases where the exposures are still in progress, only sample identification and initial weights are listed. From visual observations and weight loss measurements, high purity oxides appeared to have good corro-

sion resistance to both potassium and mercury vapor under the test conditions described. Those appearing to have the most promise include: MgO (single crystal), Al_2O_3 (sapphire, Lucalox, Coram), and Beryllia. No final weight determinations could be made on the boron nitride and aluminum nitride specimens because their unsintered condition caused heavy flaking during the cleaning operation. A visual inspection of both the sample and the potassium after exposure, however, indicated that both materials have good resistance to 850 C potassium vapor. As indicated in Table II, a sintered boron nitride piece is now on test. Attempts to sinter aluminum nitride have not been successful.

4.1.5.2 Penetration Depth and Microstructure

Studies of the penetration depth and microstructure of insulators following metal vapor exposure have been delayed until specimens formed by the coating processes are available for test. The presently available specimens, in all probability, are structurally different from the insulators being studied in the program.

Micrographs of the before and after exposure samples of the nickel clad (28%) copper conductor are shown in Figures 2 through 5. Sample WH3-B was a 340 hour re-run in mercury vapor at 538 C. Intergranular cracking of the cladding was found to a maximum depth of .0005 inches and an average depth of .00025

inches over the entire circumference. (See Figure 4.) Sample WK3 was exposed 172 hours to potassium vapor at 850 C. (See Figure 5.) Penetration of both cladding and core, and extensive "gassing" of the core were found. Gassing of the core and formation of voids as a result of the reaction between potassium and copper extended about 25% of the distance from the surface of the conductor to its center. Extensive diffusion of nickel into the copper was observed. This lowered the electrical conductivity of the copper. Grain growth in the core was not appreciable. An average grain size of .225 mm was observed both before and after exposure.

Figure 6 is a 100X micrograph of nickel plated (10%) copper wire before exposure to metal vapors. Figure 7 is a 100X micrograph of the same wire (WK-1) following 172 hours exposure to potassium vapor at 850 C. The results are similar to those reported for WK-3 with gassing being more extensive. The cladding surface was eroded and the resistance of the wire to potassium vapor was unsatisfactory. Since the nickel on the starting wire was plated on normal soft copper wire (grain size of .040 mm average), the grain growth was appreciable, (about .200 mm average). This in itself, however, is not objectionable if it causes no cladding rupture.

Figure 8 and 9 show the cross-section of Oxalloy 28, stainless steel clad copper wire before exposure to any metal vapors.

Figure 10 is a 100X micrograph of an unetched sample showing a fault in the cladding and attack on the copper core after 172 hours exposure to potassium vapor at 850 C. Figure 11 is a 100X micrograph of the same sample after it was ground down 1/32 inch and then etched. No sign of attack is visible. Figure 12 is a 250X micrograph of an Oxalloy 28 sample following exposure for 340 hours to mercury vapor at 538 C. Except for a possible slight roughening of the stainless steel cladding, the conductor was unaffected by both exposures. The isolated attack seen in Figure 10 is believed to be the result of a fault present in the cladding before exposure to potassium vapor. Grain growth was not significant. Average grain size was about .200 mm before and after exposure.

4.2 Electrical Measurements

4.2.1 Electrical Properties of Mercury and Potassium Vapor

The electrical breakdown voltages of mercury and potassium vapor have been reported and are found to obey Paschen's Law. The breakdown voltage of mercury vapor was given by Llewellyn-Jones[4] and for potassium vapor by Bratescu[5]. These values are given as a function of the product of pressure and gap. These are illustrated graphically in Figure 13.

Work done by J. F. Nolan and A. V. Phelps of this laboratory has produced data which indicates that saturated vapors may condense out on insulators to drastically reduce their surface resistivity. In their work, insulating terminals of various materials including single crystal alumina and single crystal magnesia were held at 300 C while cesium vapor pressure was increased from about 10^{-3} torr to 1 torr (saturated vapor at 300 C is about 1.5 torr). As the vapor pressure of cesium increased, the resistance of the terminals decreased from 10^{13} ohms to 1000 ohms (Al_2O_3) and 2500 ohms (MgO). When the vapor pressure was decreased to about 10^{-5} torr, the resistance of the alumina rose to 8000 ohms and the magnesia to 2.0×10^7 ohms. Of all the insulators tested, only magnesia evidenced a recovery of any major magnitude. Figures 14 and 15 show the drop in resistance as a function of terminal temperature and time.

There is some concern that the saturated potassium and mercury vapor will also condense out on the lead-in insulator. Initial tests in mercury vapor will be made where the insulator resistivity will be determined as a function of vapor pressure. A special capsule is being constructed that will allow the temperature of mercury to be slowly increased while holding the insulator at 540 C.

4.2.2 Surface Resistance versus Temperature

Figure 13 shows a plot of resistance measurements made on a sample sapphire in an atmosphere of argon to a temperature of 850 C. During these measurements, the sample (1/2 inch diameter disk about 1/16 inch thick) was suspended within a Vycor combustion tube. Evaporated gold electrodes were applied to one flate surface of the sapphire disk leaving a 1/4 inch space between. Prior to making resistance measurements, a vacuum (100 microns) was drawn on the sapphire sample and its temperature raised to 135 C for three hours. The vacuum was broken with argon gas which was then continuously swept over the sample at a rate of about one cubic foot per hour. Resistance values plotted in Figure 16 were measured with 300 volts d-c between the disk electrodes. The inverse resistance-temperature characteristic measured is essentially a volume resistance. The resistance values shown may be converted to volume resistivity in ohm-inches by multiplying by 10^{-1}.

Figure 17 is a diagram of the insulation resistance measuring apparatus. The ability of the apparatus to measure insulation resistances to values of 10^{14} ohms was demonstrated by stepwise measurements of standard resistors of values from 10^{7} to 10^{14} ohms. Moreover, the shunt resistance across the test specimen due to the test apparatus was measured as a function of temperature to 850 C. Infinite shunt resistance was indicated to 600 C and 10^{12} ohms at 850 C. The shunt resistance

is at least three orders of magnitude greater than the sapphire specimen resistance and, consequently, no error in measurement came from this source.

4.2.3 Conductivity versus Temperature

Oxalloy 28 (stainless steel clad-copper) was submitted to conductivity-temperature measurements. The sample conductor had no previous aging in metal vapor. Conductivity-temperature characteristics of the 50 mil diameter wire were determined to 538 C in an atmosphere of argon. A conventional 4-terminal measuring technique was employed in obtaining the conductivity data. Current and potential connections were made to the conductor wire with small stainless steel clamps. The wire resistance was measured with an ammeter-potentiometer. The result of this work is shown in Figure 18. Similar data were observed after the conductor had been thermally aged at 538 C for 500 hours and these points are also included in the curve. The conductivity-temperature character of a chrome-plated copper specimen is currently being measured in argon to 538 C.

4.2.4 Electrical Tests in Mercury Vapor - Insulation

4.2.4.1 Test Capsule Fabrication and Test Methods

The capsule design for the electrical tests is similar to that for the corrosion tests except that the crimped-welded end is

replaced by a lead-in insulator sealed to the capsule wall. The lead-in insulator is a disk machined to fit the I.D. of the capsule and has one or more metallic penetrations through it to provide for electrical connections. Actual fabrication of the test capsules was not completed during this quarter due to problems in making the seal between the lead-in insulator and the capsule wall.

The corrosion test results indicated that the aluminum silicate glass bond between Lucalox and tantalum was unaffected by exposure to mercury vapor at 538 C. Several attempts to make a seal between a tantalum tube and a Lucalox disk fitted to the tube I.D. were unsuccessful due to mechanical problems. Additional trials are in progress to fabricate the test capsule by this technique.

Commercial lead-in insulators sold for use on vacuum chambers are also being evaluated for use in fabricating test capsules. No conclusions as to their applicability to our problem can be made at this date.

A number of sealing techniques are under study for the potassium vapor test capsules. Any successful solutions will be also applicable to the mercury vapor test capsule. Work on techniques for making electrical contact to the samples in the capsule has been deferred until a sealed lead-in is selected.

The charging, sealing and leak testing of the capsules will be identical to that described for the corrosion test capsule. The Swagelok cap, however, will contain a 10 cc reservoir into which the mercury will be charged. The capsule will be assembled with the Swagelok end down to prevent mercury metal from contacting the sample or lead-in insulator. The test circuit described in Section 4.2.2 for tests conducted on insulation in an argon environment will be used for measuring surface and volume resistance of insulators in the metal vapor environment.

4.2.5 Electrical Tests in Potassium Vapor - Insulation

4.2.5.1 Test Capsule Fabrication and Hermetic Seals

The capsule design for the electrical tests is similar to that described in Section 4.2.4.1. Actual fabrication of the test capsules was not completed during this quarter due to problems in making the seal between the lead-in insulator and the capsule wall.

The corrosion test results indicate that a successful seal for the potassium vapor tests may be possible using a brazed joint between a disk of high purity (99.5+%) oxide and the capsule. Since the high purity oxides needed for corrosion resistance cannot be successfully metalized, the brazing must be done directly to the oxide surface. To date, wetting tests

of Nicrobraze 130, LM, CL and 60 on Lucalox in H_2, argon and vacuum have been completed. No wetting of the ceramic by the alloys took place at temperature up to 1000 C. The alloy did wet metals such as molybdenum. Exotic brazing alloys such as Zr-Ti-Be and Ni-Ti are on order for trial. Contaminating the ceramic surface to promote wetting may also be tried.

Recent work in another group at the laboratories has produced Lucalox to Lucalox and Lucalox to niobium joints using a calcia-alumina mixture and a modified aluminum-magnesium-silicate. The joints were vacuum tight (10^{-4} torr) after cooling but have not been thermally cycled or exposed to potassium vapor.

Other seal techniques under study are electron beam welding and titanium hydride bonding.

4.2.6 Aging Tests in Argon - 500 Hours

Oxalloy 28, the candidate conductor for application in mercury vapor, was subjected to thermal aging at 538 C in argon for 500 hours. During this time, the sample conductivity was measured periodically. The sample conductor had no previous aging in mercury and was tested in the "as received" condition. The measuring technique and terminal connections were the same as mentioned in section 4.2.3. The result of these measurements is shown in Figure 19. The calculated conductiv-

ity of copper at 538 C and a corresponding 67% limiting value are shown by the dashed lines. The measured conductivity of Oxalloy 28 remained quite constant throughout the 500 hour aging period and the average value (1.37×10^5 mhos per cm) is 77% of the calculated value for pure copper.

Figure 19 shows a calculated resistivity for commercial copper based on formulas and constants taken from the International Critical Tables of Numerical Data, Physics, Chemistry and Technology. An investigation of the resistivity formula contained in the National Bureau of Standards. Circular 31 "Copper Wire Tables" was also made. It is admitted by "NBS" that their formula does not take into account the slightly upward curvature of the resistance-temperature curve as observed by actual measurements. The resistivity formula taken from the "Critical Tables" does take into account a nonlinear effect and is probably more accurate than that of "NBS", particularly, at temperatures above 300 C. Thus, it seems justifiable to compare the measured resistivity of Oxalloy 28 wire to the calculated value of copper based on the "Critical Tables" formula

The resistivity of the Oxalloy 28 wire samples remained quite constant throughout the 500 hour test periods. The measured resistivity of Oxalloy 28 wire at 540 C is 131% of the calculated value for pure copper at the same temperature. Thus, isolating all parameters except temperature, assuming chemical inertness

of argon, the resistivity of Oxalloy 28 wire falls well within the specification of 150% of that of copper. The light grey metallic luster of the wire, prior to aging, changed to a dull dark grey. The conductor sample showed a weight gain of 0.03%.

4.3 Wire Coating

4.3.1 Plasma Spraying

The plasma coating equipment has just been installed and is ready for initial test runs. A number of test panels coated with various oxides are expected to be completed in the next quarter.

4.3.1.1 Conclusions

Previous experience with plasma sprayed coatings show that thin dense coatings can be obtained that are impervious to liquid metals and have good electric strength. The coating of conductors as well as overcoating statorettes appear to be very feasible.

4.3.2 Vapor Deposition at Reduced Oxygen Pressure

4.3.2.1 Equipment and Coating Techniques

The equipment used in these coating trials was a Consolidated Vacuum Corporation Metalizing unit Model E 61184. The unit has twin vertical stainless steel bell jars that are 18 inches in

diameter and 24 inches high. The unit is pumped with 6 inch oil diffusion pumps and can achieve a pressure of about 5×10^{-5} torr in relatively short pump down times.

Evaporation of aluminum at oxygen pressures of about 10^{-3} torr yields deposits which are apparently suboxides of aluminum, which oxidize to Al_2O_3 on exposure to air[6]. The rate of oxide deposition was about 1-5 Å/sec and total thicknesses of 875 Å were reported. This is a "shadowing" process. Presumably the films will not be flexible in any appreciable thickness. Also, adhesion to substrates other than aluminum is uncertain.

Attempts to deposit zirconium oxide using a pure ductile zirconium source at up to 1200-1400 C in an atmosphere of 10^{-3} torr of (flowing) oxygen yielded no measurable deposits in 2 hours. Source temperature was limited by loss of mechanical strength and consequent sagging of the source (zirconium is known to get quite weak above 862 C). The temperature was measured with an optical pyrometer.

Several attempts were made to deposit alumina from an aluminum source at about 800 C in an atmosphere of 10^{-3} torr of (flowing) oxygen. Very thin and, apparently, dense (microscopic examination) deposits were formed. The rate of deposition was lower than that expected from the DaSilva and White work[6]. Films

were not prepared for exposure tests. In the oxygen environment, the source became coated with oxide and heat transfer from the tungsten wire on tungsten wire heated alumina crucible became poor. The heater wire increased in temperature rapidly. When the oxide coating on the source was disrupted due to thermal motion of the liquid, copious quantities of aluminum would vaporize and delete the oxygen in the chamber with a resultant deposition of metallic aluminum on the target. The coating was, therefore, a mixture of Al_2O_3 and aluminum. Since no way of preventing this phenomena is apparent, no further work is planned on this approach.

4.3.3 Fusion Coatings

Mixtures of colloidal alumina and magnesia were evaluated because of their resistance as individual oxides to potassium vapor.

The mixture of magnesia and alumina was coated on the conductor and fired to 1000 C. Since this combination did not fuse, silica was added to reduce the fusion temperature. Successful coatings were obtained which fused at 1000 C. The effect of silica additions on the resistance of the combination to potassium is being determined.

4.3.3.1 Discussion of Results

Coating properties of the alumina and magnesia mix were very good. A thin uniform coating was obtained on dipping short lengths of conductor into the slurry. The fired coating was very uniform.

Compatibility of the oxide combination with stainless steel clad copper appears to be good. No adverse affect is expected.

The coating of alumina and magnesia having the silica addition adhered to the conductor very well during firing and subsequent cooling to room temperature. Bending of the coated conductor after cooling caused the coating to come off. Continuity of the coating was satisfactory but some small pinholes were evident. The pinholes were attributed to too rapid firing.

The electric strength of the coated conductors ranged from 250 to 650 volts when tested through one thickness of insulation. Higher breakdown voltages would be expected between two insulated conductors because (1) increase thickness and (2) the reduced probability of the two lowest electric strength areas being together.

4.3.3.2 Conclusions

The results to date indicate the feasibility of fusion coating of conductors for 850 C operation. The primary unknown which

will be evaluated in the near future is the resistance of these oxide combinations to potassium vapor.

4.3.4 Formation of Boron Nitride Coating

4.3.4.1 Materials and Techniques

Thermal decomposition of "B" trichloroborazole in the vapor phase with deposition of boron nitride is under investigation. Early attempts with trichloroborazole of indeterminate age gave poor results. A fresh supply of material was handled under argon as much as possible to minimize exposure to air and moisture. Radio frequency heating was used to heat the substrate and resistance heating was employed to vaporizing the "B" trichloroborazole. In runs where a gas flow was used, the substrate was located downstream from the trichloroborazole source. When a continuously pumped vacuum was employed, the substrate was positioned between the trichloroborazole ($Cl_3B_3N_3H_3$) and the vacuum coating source. The following specific experiments were done utilizing the above general technique:

(1) A tungsten rod 3/16" in diameter and 2" long was sealed under vacuum together with several grams of $Cl_3B_3N_3H_3$ in a quartz tube. The materials were positioned at opposite ends of the tube and heated. The rod was heated to 1500 C and the trichloroborazole to 113 C (vapor pressure of $Cl_3B_3N_3H_3$ = 61.1 mm)[7]. A heavy white powder formed on the quartz cradle

supporting the rod and on the walls of the quartz tube. The rod had a slight glassy white film at one end and a thicker grey film on the other. Both films covered a very small area, but were well bonded and non-conducting. The remainder of the rod was conducting on the surface.

(2) An experiment using argon as a carrier gas and a 3/16" tungsten rod substrate was performed. The rod was heated at 1050 C and the trichloroborazole heated at increasing temperatures to a maximum of 130 C. A yellowish transparent film built up over a white semi-transparent film. Both films were glassy in appearance and flaked off as the substrate cooled, leaving only a few small spots covered by a thin greyish non-ducting film.

In the subsequent experiments, a continuously pumped vacuum was used as a working atmosphere.

(3) A 3/16" diameter tungsten rod was heated to 1010 C. The trichloroborazole was heated gradually to 95 C, (vapor pressure of $Cl_3B_3N_3H_3$ 28 mm)[7]. The rod was covered with a thin film ranging from transparent to white. This film also flaked off as the rod cooled. Spots of a very thin greyish non-conducting film which adhered to the rod were left.

(4) A coil of tungsten wire was heated to 1475 C and the $B_3Cl_3N_3H_3$ was heated to 75 C (vapor pressure between 6.9 to 12.6 mm)[7]. Total time of the run was one hour. The wire was covered by a white, glassy, semi-opaque, non-conducting film that showed little tendency to flake off. The substrate, following the heat treatment, was very brittle and easily broken. The film remained on the broken pieces of wire and showed crazing in the area of the break. The film could be removed by mechanical stress or shock (Figure 20).

(5) Several tests were made on stainless steel sheathed copper wire coils to determine the feasibility of coating the wire with boron nitride. The wire coils were heated with an RF generator in a continuously pumped vacuum with no trichloroborazole present. The first coil melted near the center before a temperature reading could be taken. A second coil was taken to an indicated temperature of 1050 C as determined by an optical pyrometer. After several minutes at temperature, the coil developed a localized hot spot and melted through. Copper was vapor plated on the quartz tube. It is possible that at a slightly lower temperature and more critical temperature control, the sheathed wire can be successfully heated in this manner.

(6) A platinum wire coil was used as a substrate and heated to 1375 C in the described set up. The $Cl_3B_3N_3H_3$ was heated

to a maximum of 65 C (vapor pressure 5 mm)[7]. Total time of the run was 1.5 hours. The wire was well coated with a semi-transparent white coating which was an electrical insulator. This film was comparatively strong mechanically, but it could be flaked off by applying pressure with the fingers. (This is shown in Figure 2).

(7) A graphite rod 1/4" in diameter was used as a substrate at 1475 C. The trichloroborazole was heated at 40 C (0.6 mm pressure). Run time was 1.5 hours. The substrate had an insulating coating ranging in color from colorless to opaque white. The film was greasy to the touch and exceptionally well bonded. (Figure 21)

(8) Platinum cylinders, 3/8" in diameter, 1" long, and with walls 0.001" thick were used as substrates. The cylinders were heated to 1300 C with a maximum pressure of $Cl_3B_3N_3H_3$ of about 3.7 mm. The first cylinder was heated for 3 hours under these conditions. The interior and exterior of the tube was coated with a transparent coating of insulating quality. After a twenty minute exposure to air, the film began to pop off the cylinder. This glassy film came completely off the exterior surface of the tube after standing overnight in air. A second, shorter run of a half-hour duration was tried to see if a thinner film would be less likely to flake off. Results were identical to the first trial on platinum foil cylinders.

(9) An Inconel slab about 1 1/4" x 3/8" x 1/8" was sandblasted to give a rough surface, then washed in acetone. This substrate was heated to 1150 C in vacuum with the "B" trichloroborazole at a temperature of 50 C. After a 25 minute run, the RF generator cut out. The surface of the slab was covered with a light tan coating and a few small, crystalline white spots, which possibly could be condensed $Cl_3B_3H_3N_3$. Testing the slab with a resistance meter showed metallic conduction. The run was repeated using a sandblasted slab of Inconel which was etched in HCl, washed and dried. The trichloroborazole was the same material used in the previous run. A three hour run with the substrate at 1135 C and the $Cl_3B_3N_3H_3$ at 60 C gave results similar to the first run except that there were no white spots present. The slab was covered with a flaky deposit ranging in color from tan to brown which conducted an electric current. A third trial using a sandblasted, acid etched, Inconel slab and fresh "B: trichloroborazole was made. After running for 4 1/2 hours under the previous experimental conditions, similar results were obtained. A black, insulating film flaked off. The substrate was colored in various shades of brown, and its surface was conducting.

(10) Twenty mil tungsten wire, wound in a short coil was heated to 1050 C for half hour in a vacuum with trichloroborazole. The $Cl_3B_3N_3H_3$ was not heated. After cooling in the vacuum, the thin transparent film on the coil began to peel and pop off the wire after a short exposure to air. A repeat of this run with the substrate heated to 1115 C, the trichloroborazole to 60 C, and a duration of 6 hours was made. The coil was again vacuum cooled. Flaking and popping of the film occurred a short time after air exposure. The films deposited on the tungsten wire were transparent and insulating. Cooling of the substrate was slow to avoid thermal shock. Flaking and popping seemed most pronounced on the outer surfaces of the smaller radius turns.

The heating techniques followed in these experiments was to heat the substrate first and to cool it as gradually as possible after the trichloroborazole had been cooled. This was done to prevent any "B" trichloroborazole from condensing on the decomposition product deposited on the substrates.

4.3.4.2 Discussion of Results

Films deposited at higher temperatures appeared to adhere better than those formed at lower temperatures. The films formed at lower temperatures seemed to cover the substrates more uniformly than the high temperature films, which tended to have a thick coating on the end facing the trichloroborazole

and a thinner or no coating on the other end. However, this appears to be a problem of tube geometry. When wire coils are used, the radius of the curve appears to influence the adhesion of the film somewhat. The film flakes most easily from small radius outside curves. In cases where the substrate was heated at higher temperatures, there was a tendency for the film to be thicker on the end nearest the trichloroborazole.

Boron nitride formed at lower temperatures is glassy in nature and has short range order when compared to highly oriented boron nitride obtained at 1900 C. This makes X-ray analysis of the reaction products difficult. Because of the small amount of the film present, chemical analysis is also difficult. Infrared analysis is being investigated.

Film thickness can be controlled by the time and vapor pressure of trichloroborazole. Uniformity of thickness appears to be a function of the tube geometry. Chemical cleaning was used to prepare the substrate surfaces for plating. In most cases, the surfaces were smooth. There was no chemical etching. It is possible that the condition of the surface has some influence on adhesion of the film.

4.3.4.3 Conclusion

This method of coating may be feasible if it is possible to heat the substrate to a high temperature. There may be considerable difficulty in coating conductors because of the relatively low melting points. It is planned to evaluate the effect of surface treatment on the adhesion of the BN coating to the substrate.

4.3.5 Formation of Alumina by Thermal Decomposition

4.3.5.1 Materials and Techniques

Several unsuccessful attempts were made to vapor deposit alumina on spirals of tungsten and platinum wire. The source material was aluminum isopropoxide which has a melting point of 119 C and a vapor pressure of about 0.3 mm at 100 C. The isopropoxide was used because it contains the required amount of oxygen to produce Al_2O_3, it is relatively volatile and a pure sample was available. The apparatus consisted of a straight quartz tube in which was placed one porcelain boat containing the isopropoxide and another, about 8 inches farther downstream in the tube, containing the wire spiral. A heating tape was used to heat the portion of the tube containing the isopropoxide, while the wire spiral was heated with a radio frequency coil which surrounded the quartz tube at the location of the spiral.

Initial runs were made using an argon flow to carry the isopropoxide vapors across a tungsten spiral heated to 1400 C. One possible and desirable mode of decomposition of aluminum isopropoxide is given by the following equation:

$$2\ Al\ (O\ C_3H_7)_3 \rightleftharpoons Al_2O_3 + 6\ C_3H_6 + 3\ H_2O$$

As the isopropoxide decomposed upon coming in contact with the hot wire, the alumina might be expected to deposit on the wire while the hydrocarbon and water would be carried off in the argon flow. Further cracking of the hydrocarbon might occur giving methane and acetylene or ultimately carbon and hydrogen. Apparently, severe cracking did occur, for considerable amounts of carbon collected on the relatively cool quartz tube and porcelain boat. Most of the carbon growth was covered with a white deposit which was probably alumina. Conditions of the experiment (rate of argon flow, rate of evaporation of the isopropoxide and temperature of the spiral substrate) were changed in several experiments but no insulating film was obtained. A cross-section of the wire showed that there was some attack on the tungsten surface, probably by carbon.

With the intention of preventing the formation of carbon, similar experiments were carried out using an oxygen flow in place of argon and a platinum spiral in place of tungsten. The amount of carbon formation was lessened but was still very much

in evidence and again it was covered with what is believed to be Al_2O_3. No insulating film was formed on the wire.

Use of aluminum methoxide as a source material is being considered as a means of minimizing or eliminating the carbon problem. Another possibility, blowing the fairly volatile aluminum chloride over a hot substrate by moist argon might deposit Al_2O_3 on the substrate. Another refractory insulator worthy of consideration is aluminum nitride. It is reported that the aluminum chloride-ammonia complex ($Al\ Cl_3 \cdot NH_3$), can be decomposed to aluminum nitride.[10]

4.3.6 Formation of Aluminum Fluoride

4.3.6.1 Materials and Techniques

A process for coating an aluminum substrate with aluminum fluoride by reaction with fluorine and/or hydrogen fluoride has been developed by Bell Laboratories[8][9]. Such coatings are flexible and not limited in thickness by diffusion rates as in Al_2O_3 formed by direct aluminum oxidation. Coatings of 5 microns thickness have been made by Bell Labs. Such coatings can be oxidized to Al_2O_3, over the outer 1000 Å of their thickness by heating to 550 C in air. They might possibly also be converted to aluminum nitride by heating in ammonia. All of these reactions are non-shadowing and could be carried out on essentially finished wound coils.

According to calculations, the aluminum fluoride itself would be thermodynamically unstable to potassium vapor above 550 C, but the alumina oxide or aluminum nitride might protect it.

Aluminum nitride (AlN) in the reasonably pure, dense state has a specific resistivity of about 10^6 ohm-cm at 850 C[10]. Sintering temperature for AlN is 1950-2050 C, as reported by Alcoa Labs. Experiments in crystal growing on AlN from vapor elsewhere in these labs have not been successful. Also, of course, one may expect AlN to be rather sensitive in its resistivity to doping with impurities.

Equipment for treatment of aluminum films on Inconel substrate with HF or F_2 at 500 C is nearly ready. (This process was developed by Bell Labs and is at present reported to be worked on by Allied Chemicals.) The reaction intended is:

$$2Al^{o} + 6HF \rightleftharpoons 2AlF_3 + 3H_2$$

The AlF_3 layer is reported to be a good insulator probably up to 850 C. It is reported to be flexible. However, calculation has shown that AlF_3 is thermodynamically unstable in potassium. Therefore, it is intended that the AlF_3 formed

will be partly or wholly converted to Al_2O_3 by direct oxidation. It is hoped that a thin layer of AlF_3 left under the converted Al_2O_3 will serve as a flexible "slip layer" to equalize expansion coefficients, yet be protected from potassium by the Al_2O_3.

4.3.7 Densification of Porous Coatings by Mass Transport

4.3.7.1 Materials and Techniques

The high sintering temperature required to produce high density structures of high purity is a major problem presented by most of the promising candidates. Since the rate of sintering at any given temperature is generally limited by the rate of material transport, rate increases may be possible by use of an intergrain medium in which the material to be densified has relatively high solubility and mobility under the experimental conditions employed, allowing it to follow a thermal or other energy gradient. The principle is used in "hydrothermal" crystal growth of silicon dioxide. A possible solution has been found to the problem of accelerating material transport rates of refractory oxides to achieve a dense structure without raising the temperature above the limits of the wires to be used. Work done in this laboratory by Dr. T. L. Chu indicates that reaction equilibria such as:

$$Al_2O_3 \text{ (solid)} + 6HCL \text{ (gas)} \rightleftarrows 2 \text{ Al } Cl_3 \text{ (gas)} + 3H_2O \text{ (gas)}$$

are able to achieve rapid transport. The equilibrium constants for the above reaction are:

800 K	10^{-20}
1000 K	10^{-16}
1200 K	10^{-14}

For beryllium oxide with hydrogen chloride the equilibrium constants are:

800 K	3.2×10^{-9}
1000 K	5.7×10^{-8}
1200 K	1.8×10^{-6}
1400 K	2×10^{-5}

Both groups of data indicate that the refractory oxide will be transported from a hotter to a colder region of the system. The transport rate will be a function of the hot-cold temperature differential, distance or path length, and hydrogen chloride pressure. Apparatus is being set up in which a wire coated with finely divided refractory oxide will be placed in hydrogen chloride gas at 10-15 atmospheres of pressure. The aggregate will be heated from the outside (periphery of the coated wire) and the end of the wire will be taken out to a cool zone so that a temperature gradient will exist across the granular insulation. We expect this system to show a net

transport of refractory oxide from the outer granules of the coating to the inner, cooler layers where it will deposit as crystalline or,at least, dense material.

One preliminary experiment has been made. A quartz tube of 1" I.D. and 30 cm length was loaded with 6 g of Al_2O_3powder (Alcoa T1-6, 99.5 + % Al_2O_3, 0.03% Fe) at one end and a holder for three quartz slides at the other. The tube was charged with 0.6 g dry hydrogen and sealed. The charge was calculated to yield a pressure of about 10 atm. at 800 C. Half of the tube was inserted into a tube furnace and the other half (containing the target slides) left outside. At temperatures of 400 C and 700 C in the furnace, reaction was very slow. At a 1000 C hot end temperature, an estimated 0.05-0.10 g of white solid was transported to the cool tube end, a minimum distance of 15 cm. The target slides showed 0.015, 0.008 and 0.004 g deposits. The deposits on target slides and tube wall were not dense or transparent. The remaining Al_2O_3 source powder was not sintered, but had turned dark grey.

It appears that alumina was purified of Fe in transport. This will be confirmed by analysis. The densest coatings achieved, as well as some of the heaviest, were in the hottest deposit zone. The next trial will be with shorter transport path length and lower Δ T.

4.3.8 Potting Compositions

Potting compounds in this program on the development of metal vapor resistant conductors have been considered initially as a back up in case wire coatings are not satisfactory. However, in addition to a back up material added protection from metal vapors would be given. Other advantages are more evident on statorettes or actual equipment. The resistance to damage by vibration and mechanical shock are greatly improved by potting the conductors. A very definite improvement in thermal conductivity is also obtained.

Several potting compounds were suggested as candidates for use at temperatures up 850 C because of their good insulation resistance. These are the first five materials listed in Table III. Since there is some indication that the binders for these compounds might be affected by potassium vapor, other compounds (6 through 9) were formulated using collodial oxides as binders. Samples have been prepared for tests in the two vapor environments.

The results indicated that at least one new potting compound was sufficiently strong after firing to be a candidate for further testing. It was expected to be more resistant to potassium vapor because it contained only alumina and zirconia.

4.3.9 Discussion of Wire Coating Methods

The advantage of all coating methods under consideration are their reported or indicated ability to form dense, non-porous coatings. The boron nitride process should be adaptable to continuous coating techniques but present formation temperatures exceed the melting point of the conductor core. However, recent references indicate a boron nitride coating can be formed at lower temperatures (less than 1000 C).

Vacuum deposition of oxides in partial pressures of oxygen appears to yield a good coating but non-uniformity of deposition rate has resulted in aluminum contamination in the deposits. The transport method of depositing alumina using hydrogen chloride has failed to deposit a dense coating.

Fusion coatings still appear to be one of the best possibilities for mercury vapor environments. In addition, fusion coating methods appear practical as a means of getting a potassium resistant ceramic insulation on the surface of a conductor.

A high rate of effort will be continued in the areas of boron nitride vapor deposition and fusion coating techniques.

V. PROGRAM FOR NEXT QUARTER

5.1 Corrosion Studies

Additional exposure tests will be run during the next quarter. When the Inconel clad silver and nickel clad silver conductors are received, samples will be exposed to potassium vapor at 850°C. Samples of insulators which were unaffected in the first series of vapor exposures will be rerun in shapes more suitable for "after exposure" electrical measurements. Insulated wire and insulated coupon specimens will be exposed to metal vapor as they become available from the coating process trials. Exposure tests will be made on the zirconia-alumina potting compound and any others which appear promising during the next quarter.

5.2 Electrical Tests in Argon

"Before" and "after" exposure resistivity measurements will continue being made in argon at elevated temperatures on insulator materials that had good resistance to the metal vapor in the first test series. Oxalloy 28 conductor samples will be aged at 850°C in argon for 500 hours and periodic conductivity measurements will be made. Conductivity-temperature characteristics of the Inconel clad silver and nickel clad silver will be determined as well as the effects of 500 hours aging at 850°C.

5.3 Electrical Tests in Metal Vapor

Electrical test capsules will be prepared first for mercury vapor

exposure. The initial tests will be devoted to determining the resistance of the lead-in insulator as a function of the mercury pressure in the capsule. The lead-in insulator will be maintained at 538°C as the mercury reservoir temperature is increased to affect the increase in mercury vapor pressure. The data collected will be used to calculate the test sample resistance in future tests and to determine if the saturated vapor environment selected for the test condition is unsuitable. Following fabrication of the electrical test capsules for potassium;surface and volume resistance will be measured on solid insulator specimens and on insulation coated specimens. Electric strength of the coating on the insulated conductors will also be determined.

Test capsules for electrical tests in mercury vapor will be fabricated using commercial lead-in insulators (vacuum chamber lead-ins, etc...) and specially prepared lead-ins using aluminum silicate glass seals. Test capsules for electrical tests in potassium vapor will be fabricated using the seal technique which appears most promising during the tests to be conducted early in next quarter. The seals to be evaluated are: calcia-alumina seal, Zr-Ti-Be brazed joint, Ni Ti brazed joint, TiH_2 bonded joint and electron beam welded joint.

5.4 Coating Studies

Attempts will be made to formulate coatings with low silica contents. Coatings containing zirconia, thoria and beryllia will also be considered.

Surface treatment of substrates will be investigated to increase adhesion of boron nitride, particularly during exposure to air. Stainless steel (410), Inconel and nickel substrates will continue to be investigated.

Decomposition of aluminum methoxide and decomposition of aluminum chloride in moist argon will be attempted as a means of forming alumina. Vacuum deposition of alumina and wet and gaseous anodization of aluminum will be investigated as other possible methods for forming alumina on conductors.

Mass transport of alumina will be attempted through porous pieces of alumina. If these trials are successful,the trials will be continued on porous coatings on wire. The technique will be investigated for magnesia and beryllia.

Attempts will be made to form aluminum fluoride on aluminum clad or coated conductors. If the attempts are successful,attempts will be made to form an alumina or aluminum nitride sheath on the AlF_3 coating to provide the necessary corrosion resistance.

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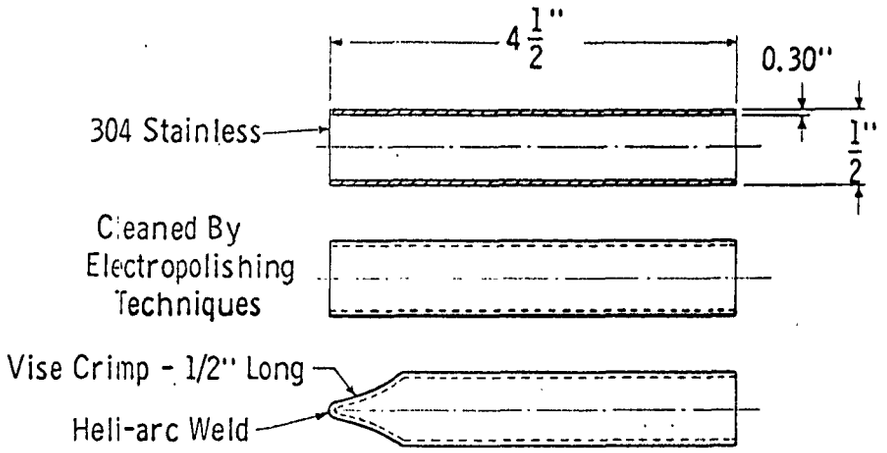
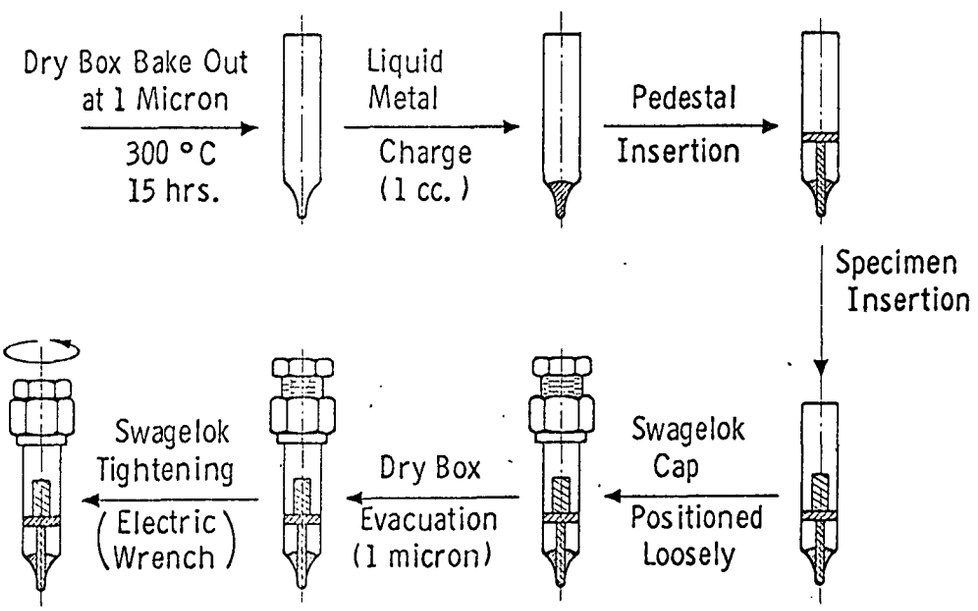
DWG. 626A200

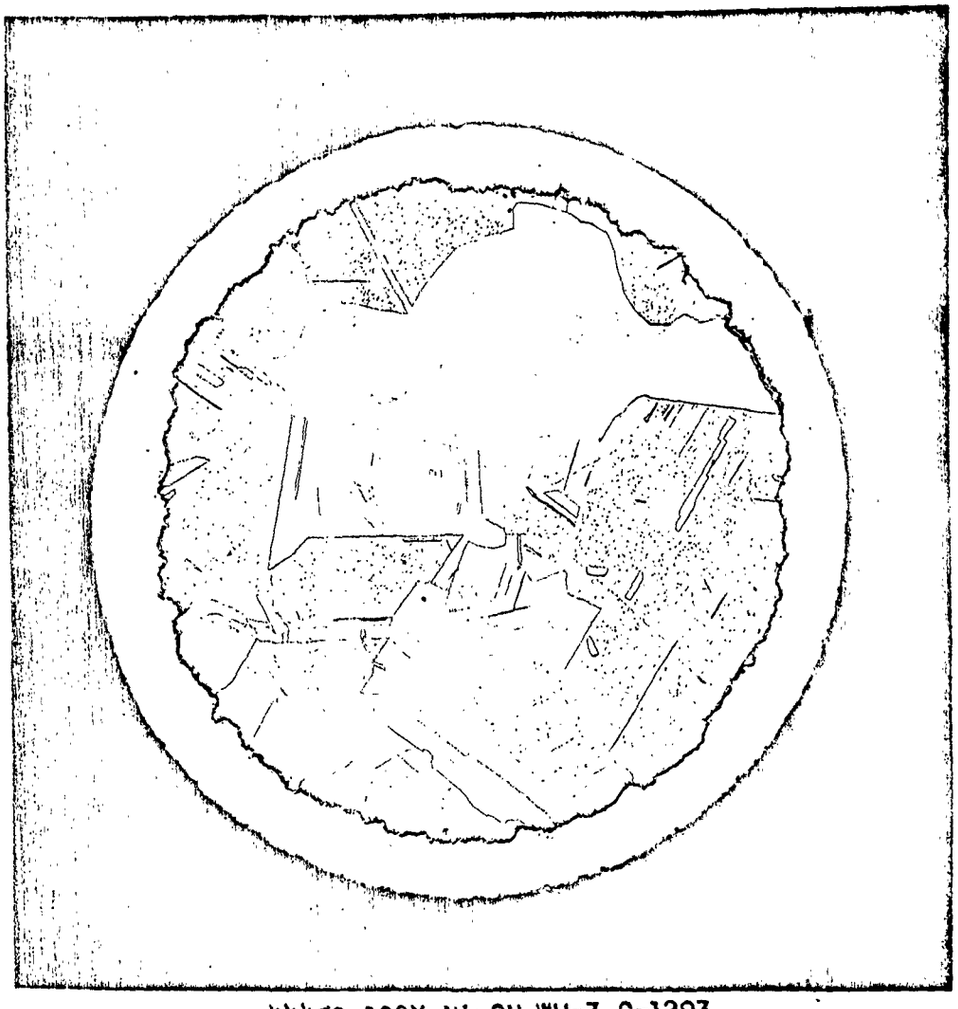


Note: Weld is leak checked with helium after heating to cherry red with oxy-acetylene torch.



Note: Pedestal, Sample & Swagelok baked out at 300 °C - 1 micron 15 hrs.

Fig. 1—Cleaning and sealing technique for corrosion test capsules

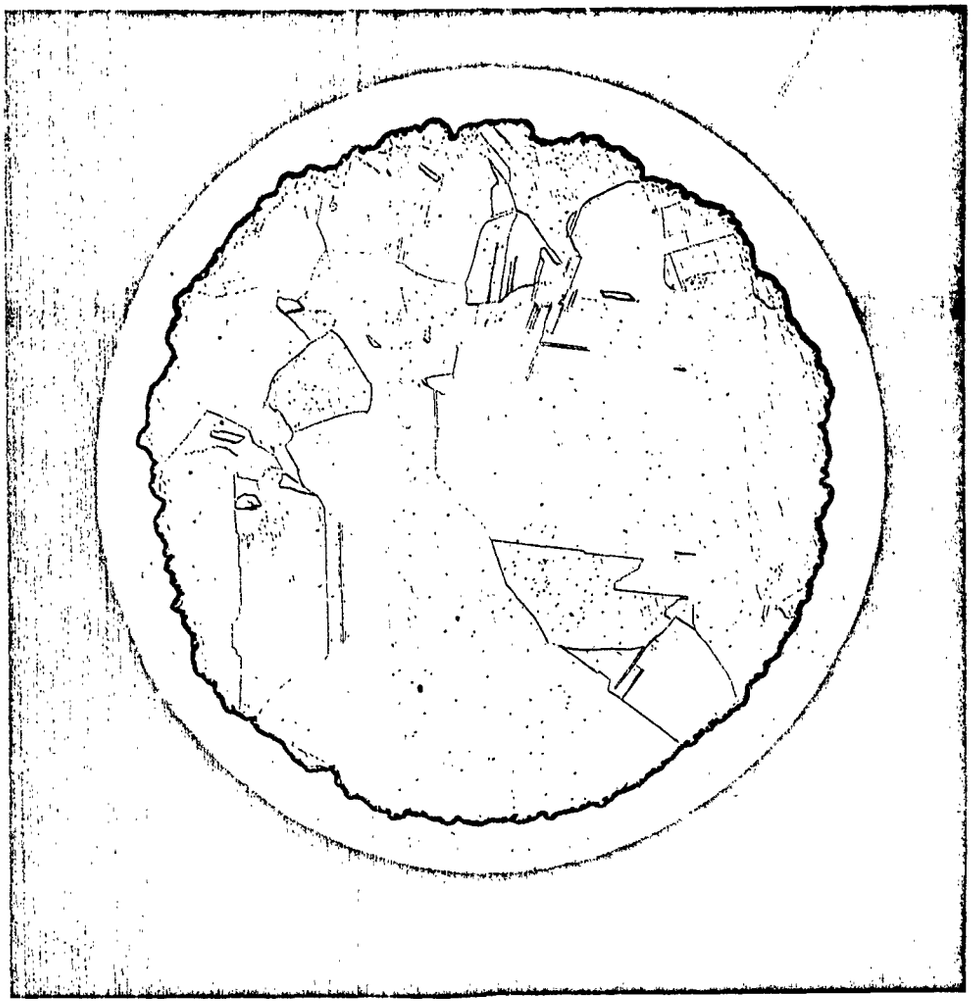


44480 100X Ni-Cu WH-3 C-1293

Figure 2

Neg. No. 44480

Nickel Clad (28%) Copper Wire Before Metal Vapor
100X Ni-Cu WH-3B C-1293

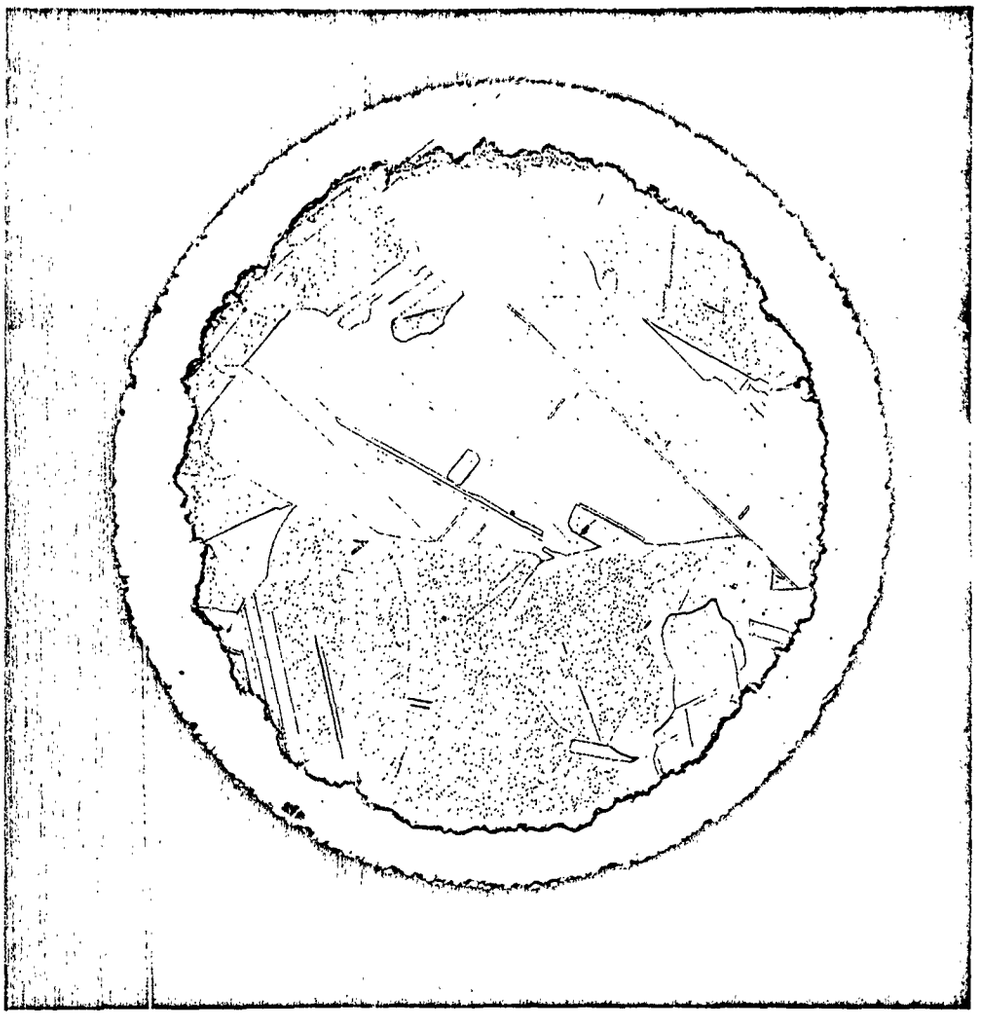


44474 100X NI-CU WK-3 C-1145

Figure 3

Neg. No. 44474

Nickel Clad (28%) Copper Wire Before Metal Vapor Exposure - 100X Ni-Cu WK-3 C-1145



44481 100X NI-CU WH-3 C-1293

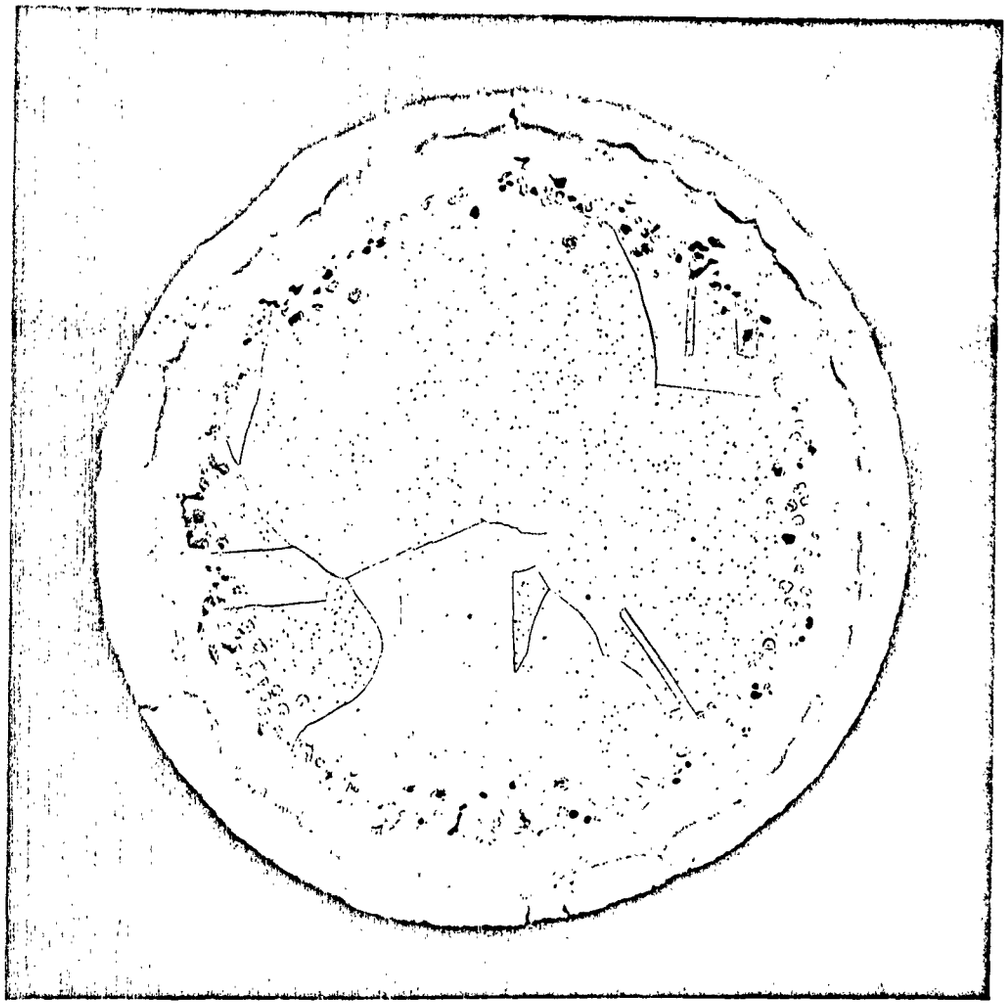
Ref

4

Figure 4

Neg. No. 44481

Nickel Clad (28%) Copper Wire After 340 Hours
Exposure to Mercury Vapor at 538°C - Second Series of Tests
100X Ni-Cu WH-3B C-1293

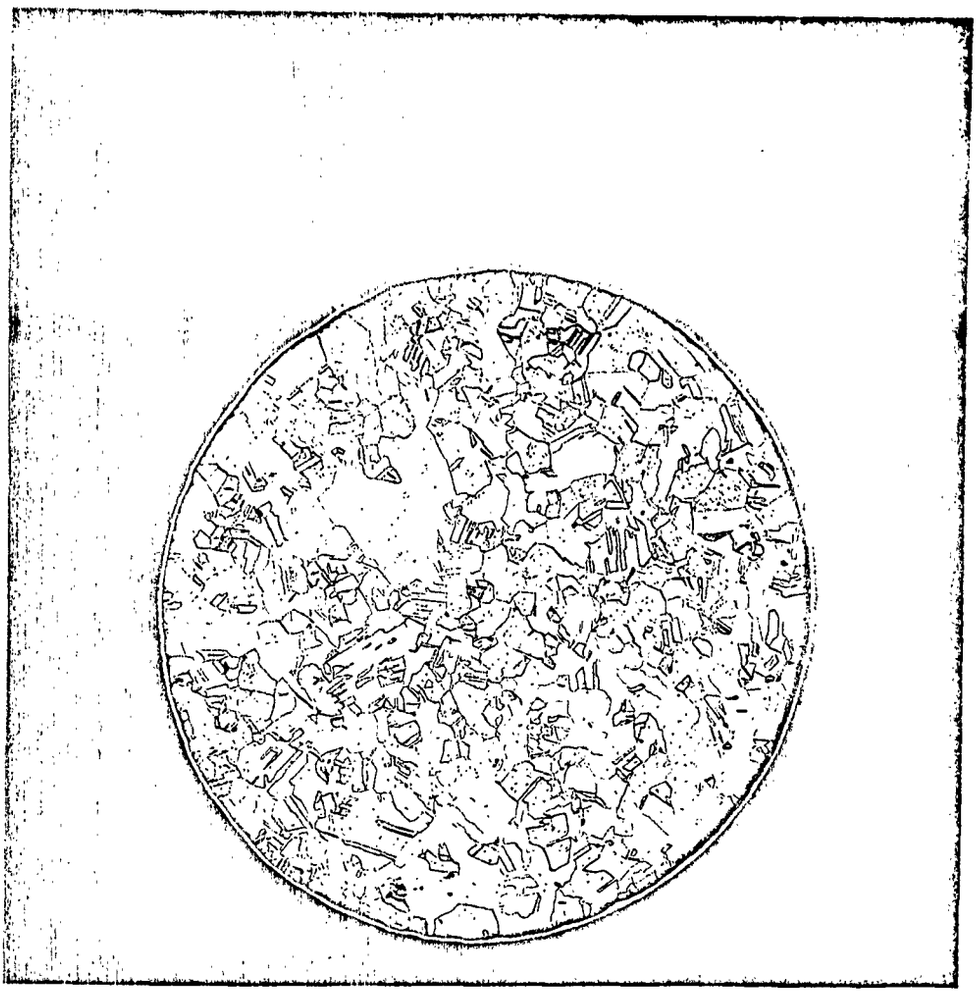


44475 100X NI-CU WK-3 C-1145

Figure 5

Neg. No. 44475

Nickel Clad (28%) Copper Wire After 172 Hours
Hours Exposure to Potassium Vapor at 850°C
100X Ni-Cu WK-3 C-1145

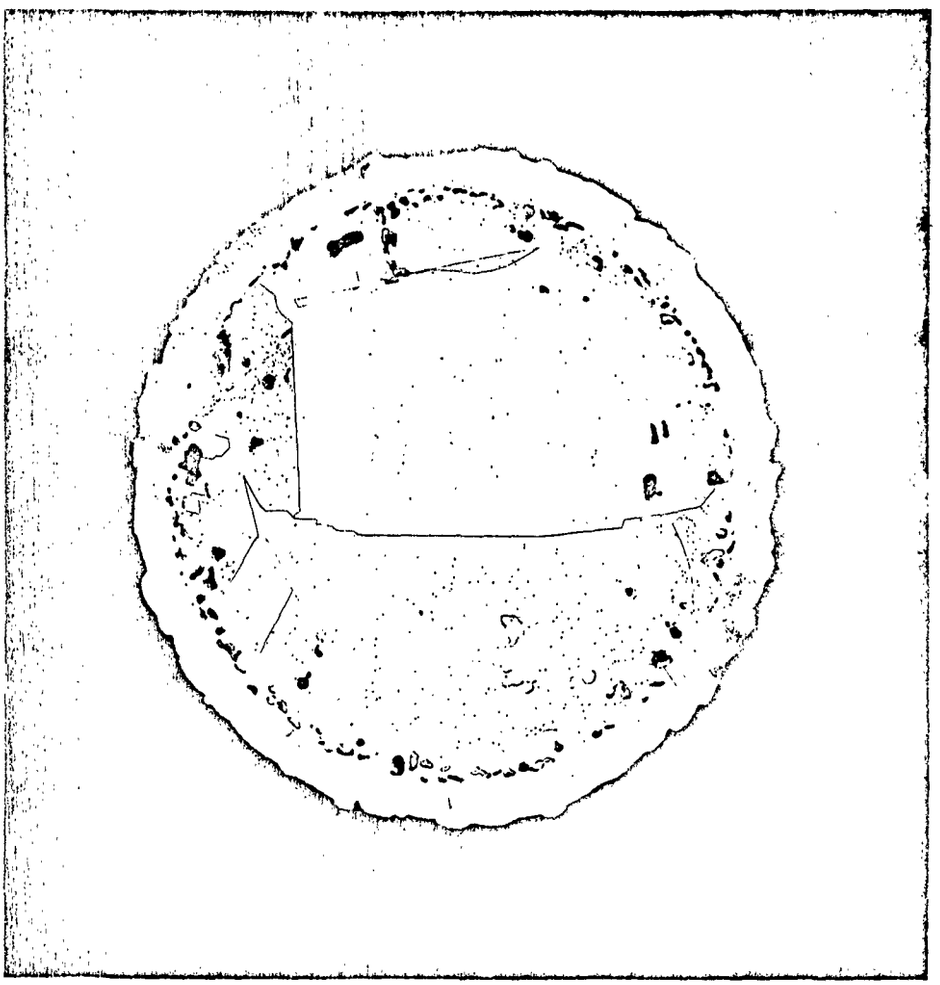


44476 100X NI-CU WK-1 C-1146

Figure 6

Neg. No. 44476

Nickel Plated (10%) Copper Wire Before Metal Vapor Exposure - 100X Ni-Cu WK-1 C-1146

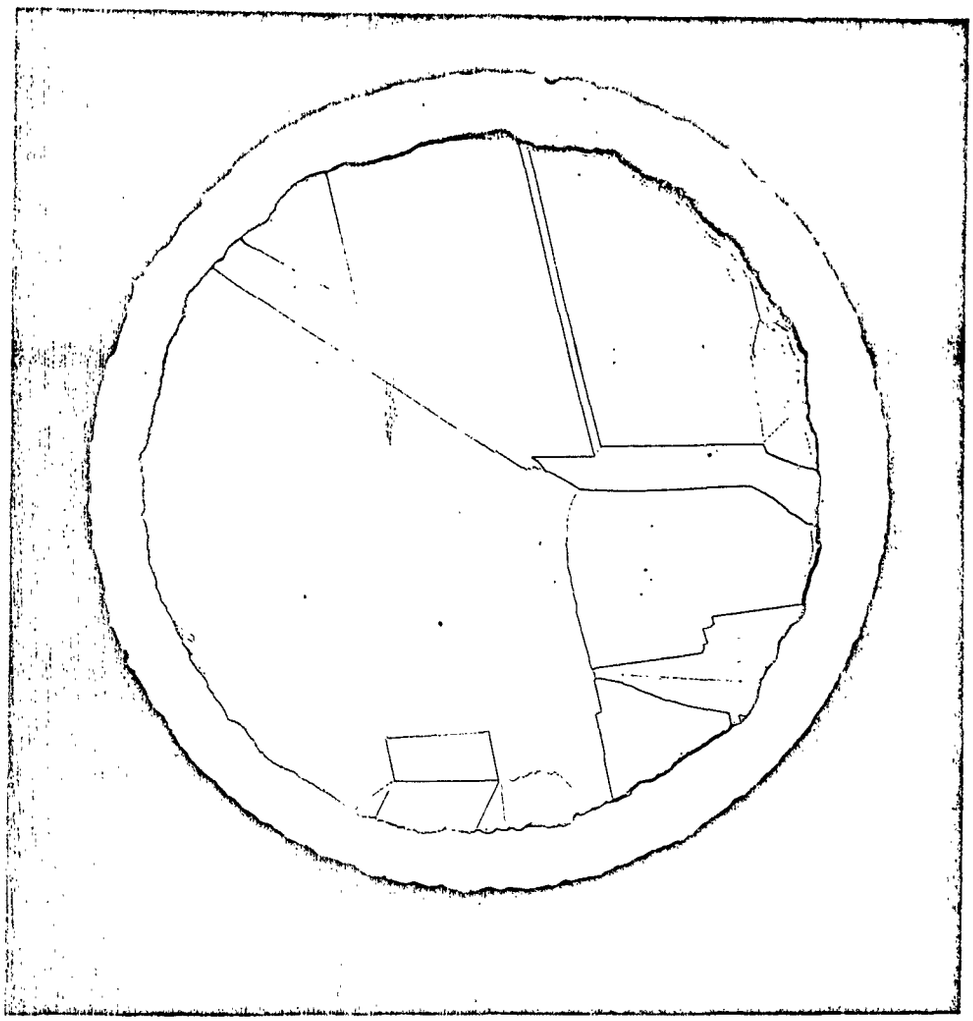


44477 100X Ni-Cu WK-1 C-1146

Figure 7

No. 44477

Nickel Plated (10%) Copper Wire After 172 Hours
Exposure to Potassium Vapor at 850°C
100X Ni-Cu WK-1 C-1146



44478 100X NI-CU WK-5 C-1147

Figure 8

Neg. No. 44478

Oxalloy 28, Stainless Steel Clad (28%) Copper Before Metal Vapor Exposure - 100X Oxalloy WK-5 C-1147

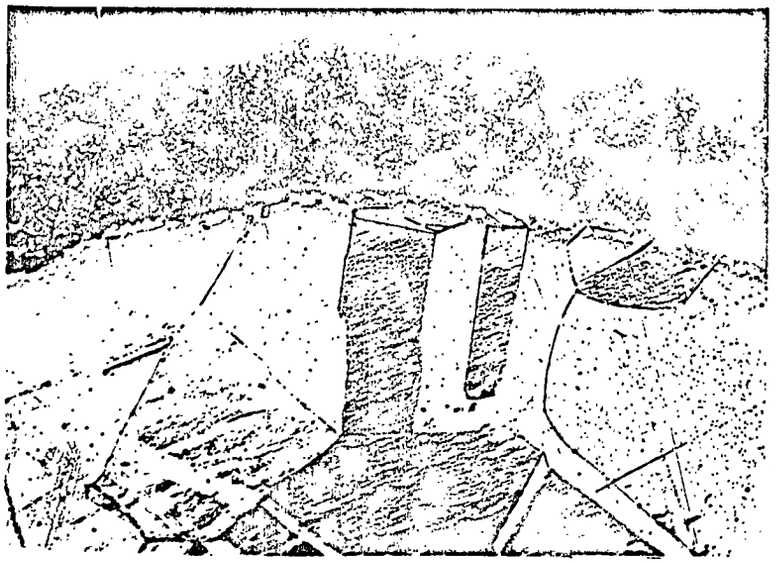
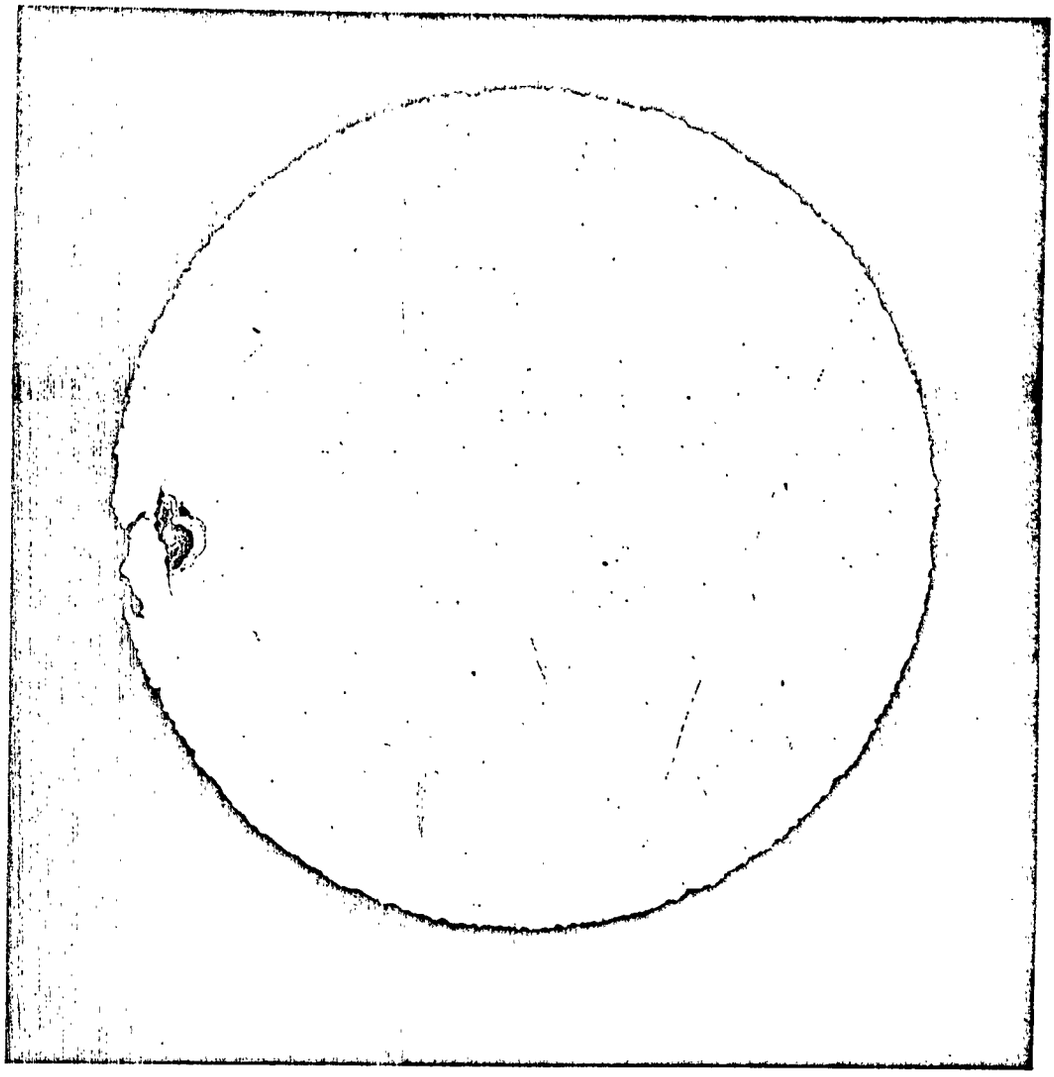


Figure 9

Neg. No. 44030

Oxalloy 28, Stainless Steel Clad (28%) Copper Before Metal Vapor Exposure 250X SS Clad CU-S C-0982

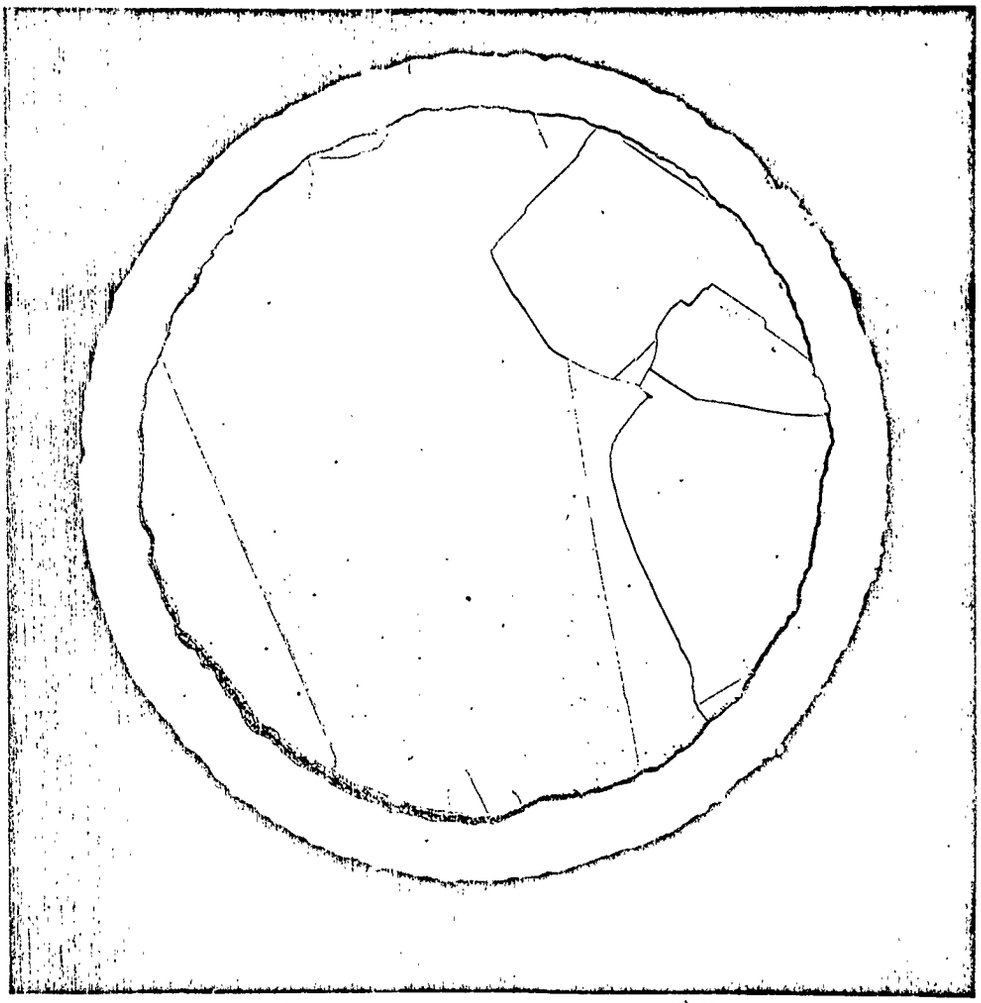


44185 100X .28 S.S. CLAD CU WIRE TREATED WK-5 C1147

Figure 10

Neg. No. 44185

Oxalloy 28, Stainless Steel Clad (28%) Copper After 172 Hours Exposure to Potassium Vapor at 850°C. Sample Unetched - 100X .28 SS Clad Cu Wire Treated Wk-5 C-1147



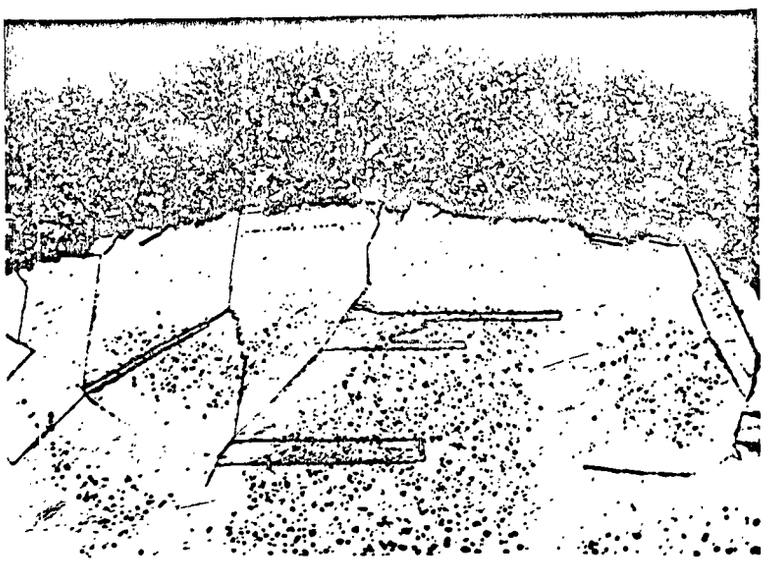
44479 100X NI-CU WK-5 C-1147

11

Figure 11

Neg. No. 44479

Oxalloy 28, Stainless Steel Clad (20%) Copper After 172 Hours Exposure to Potassium Vapor at 850°C. Sample Etched - 100X Oxalloy WK-5 C-1147



44031 250X SS CLAD CU-7 C-0982

Figure 12

Neg. No. 44031

Oxalloy 28, Stainless Steel Clad (28%) Copper After 340 Hours Exposure to Mercury Vapor at 538°C - 250X SS Clad CU-7 C-0982

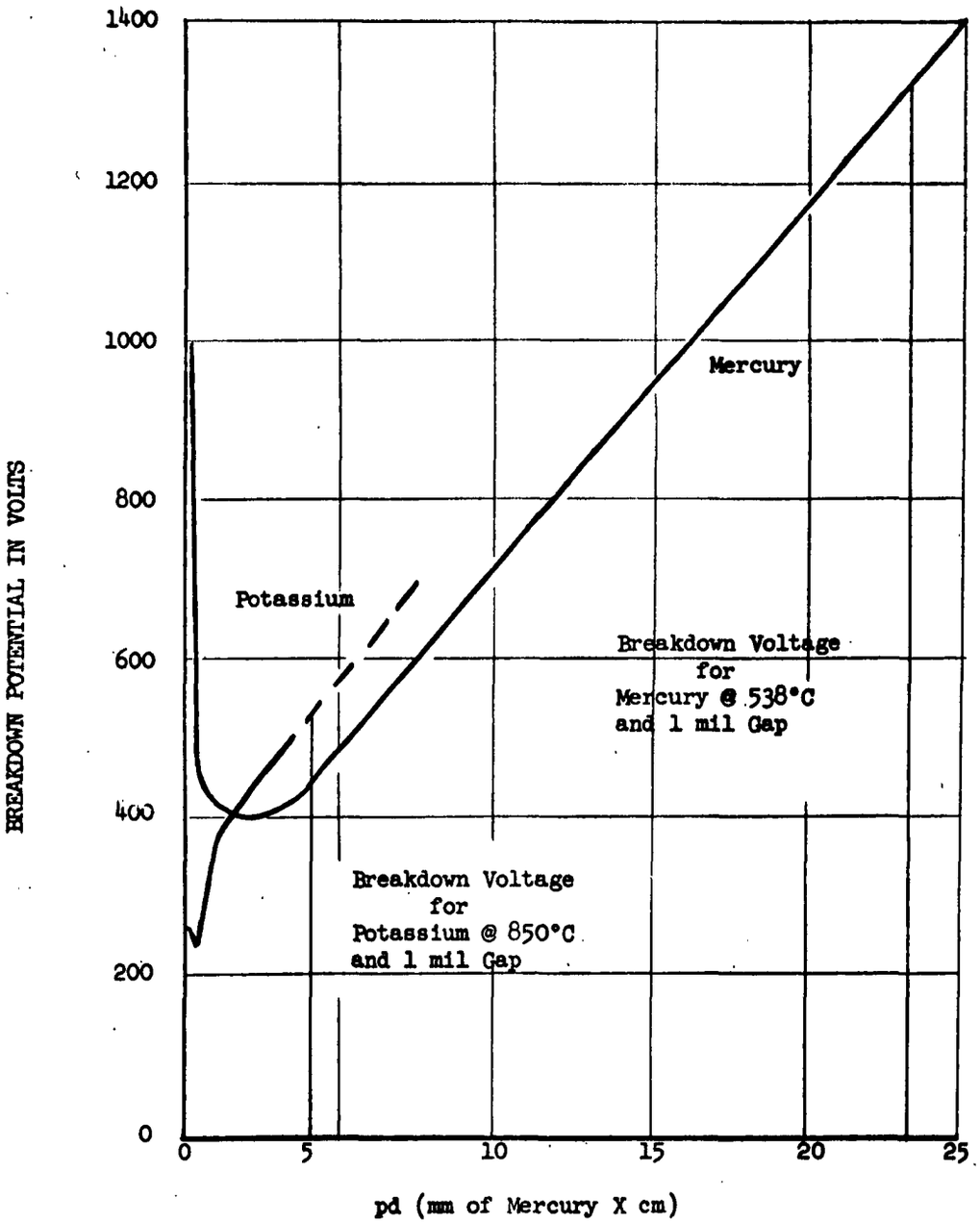


Fig.13 Paschen Curves for Mercury and Potassium Vapor

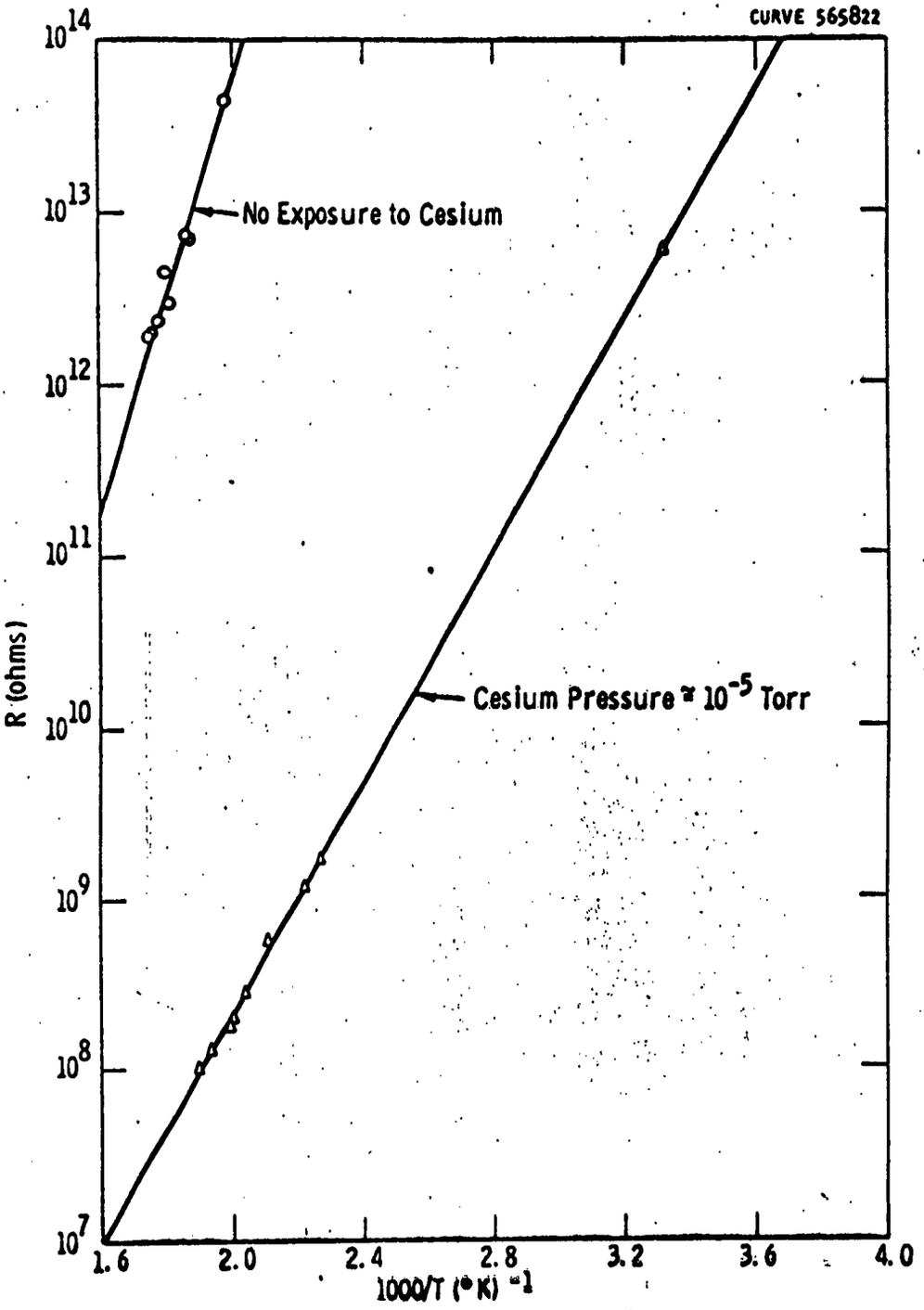


Fig. 14 Leakage Resistance of MgO Terminal vs. $\frac{1}{T}$ where T is the Temperature of the Terminal in °K. The Upper Curve is for No Cesium Exposure; The Lower Curve for a Cesium Vapor Pressure of About 10^{-5} Torr.

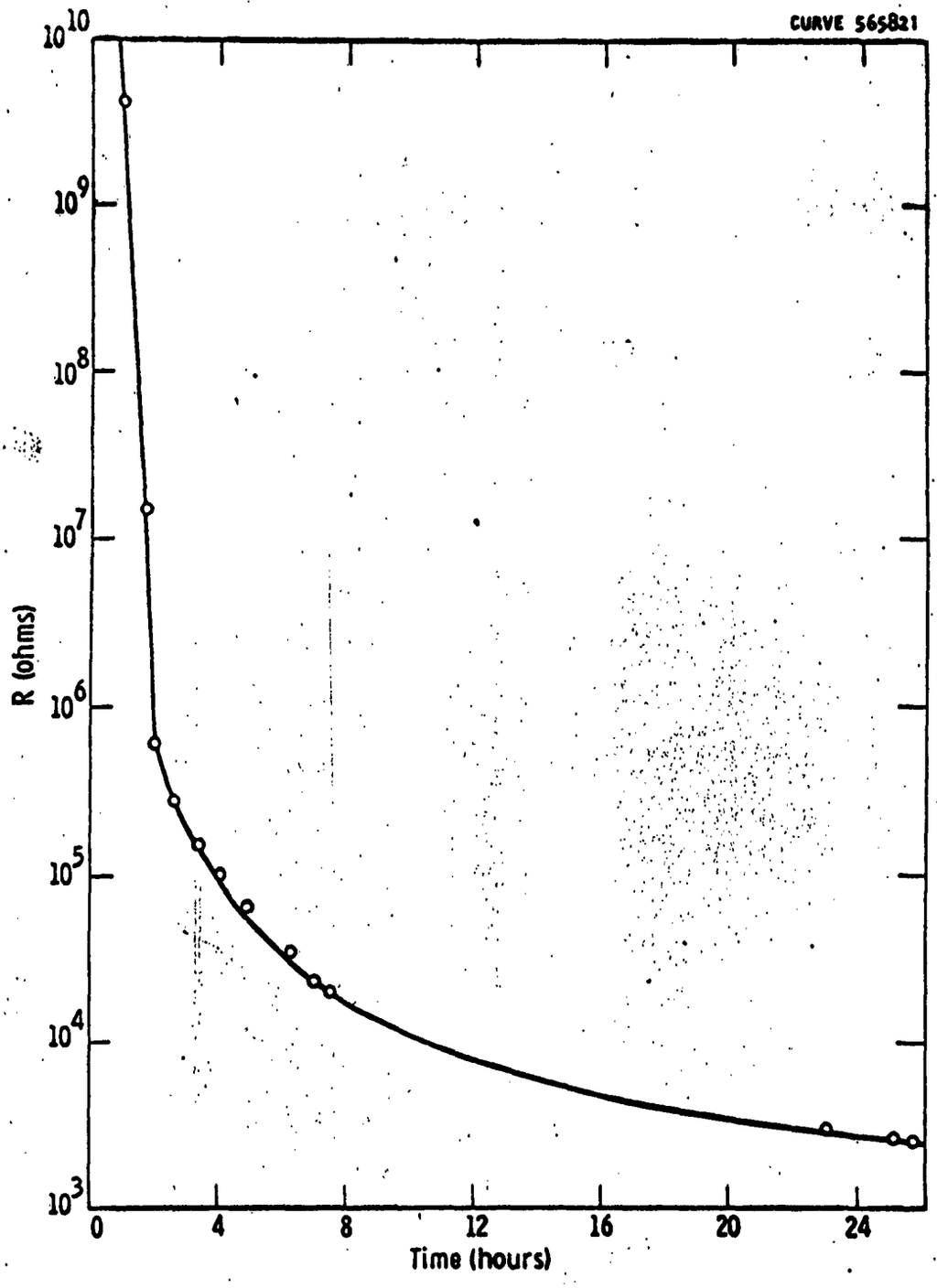


Fig. 15 Leakage Resistance of MgO Terminal as a Function of Time After Cesium Reservoir is Raised to Give a Vapor Pressure of 1 Torr. The value of R at Time = 0 is 2×10^{12} ohms.

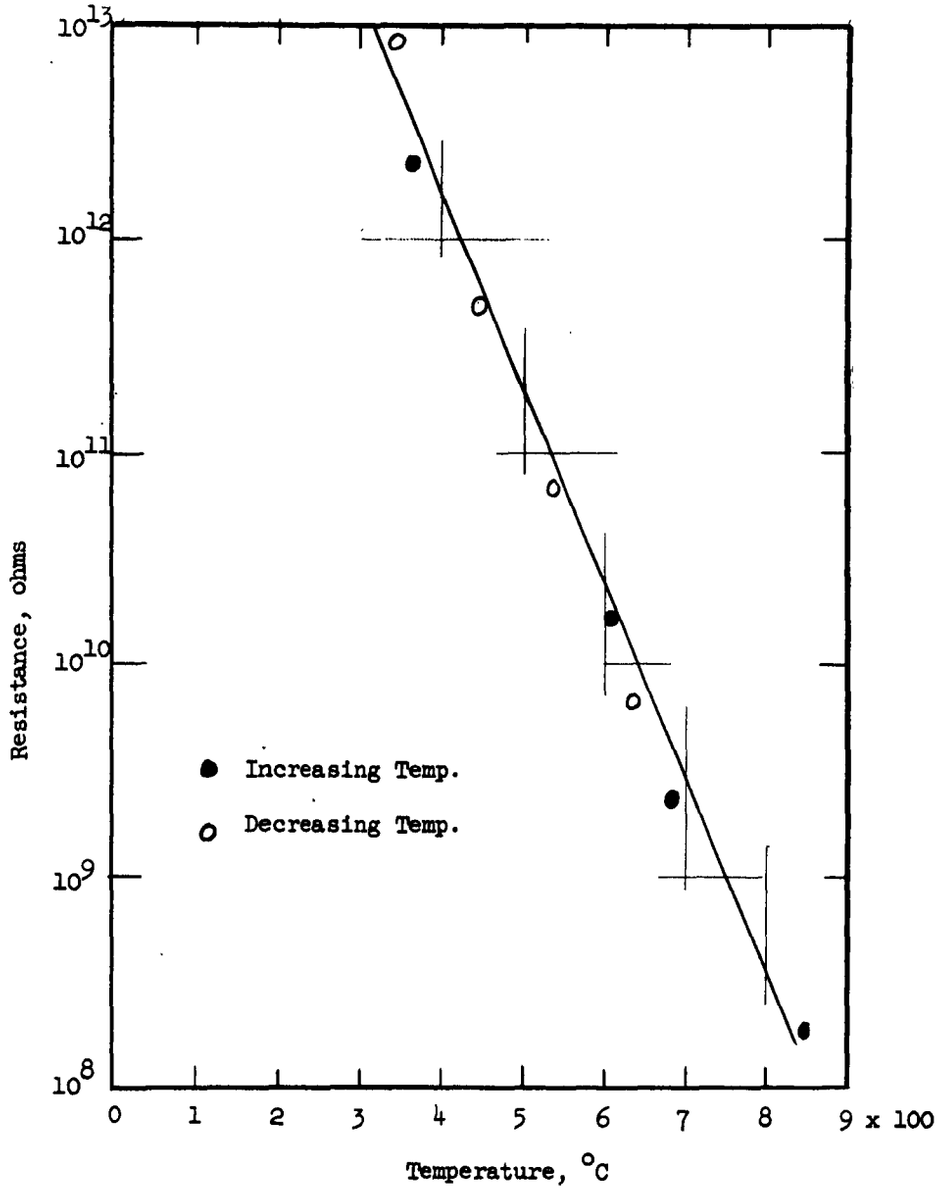


Figure 16. Resistance - Temperature Characteristics of Sapphire in Argon.

(1/2" dia. disk - 1/16" thick)

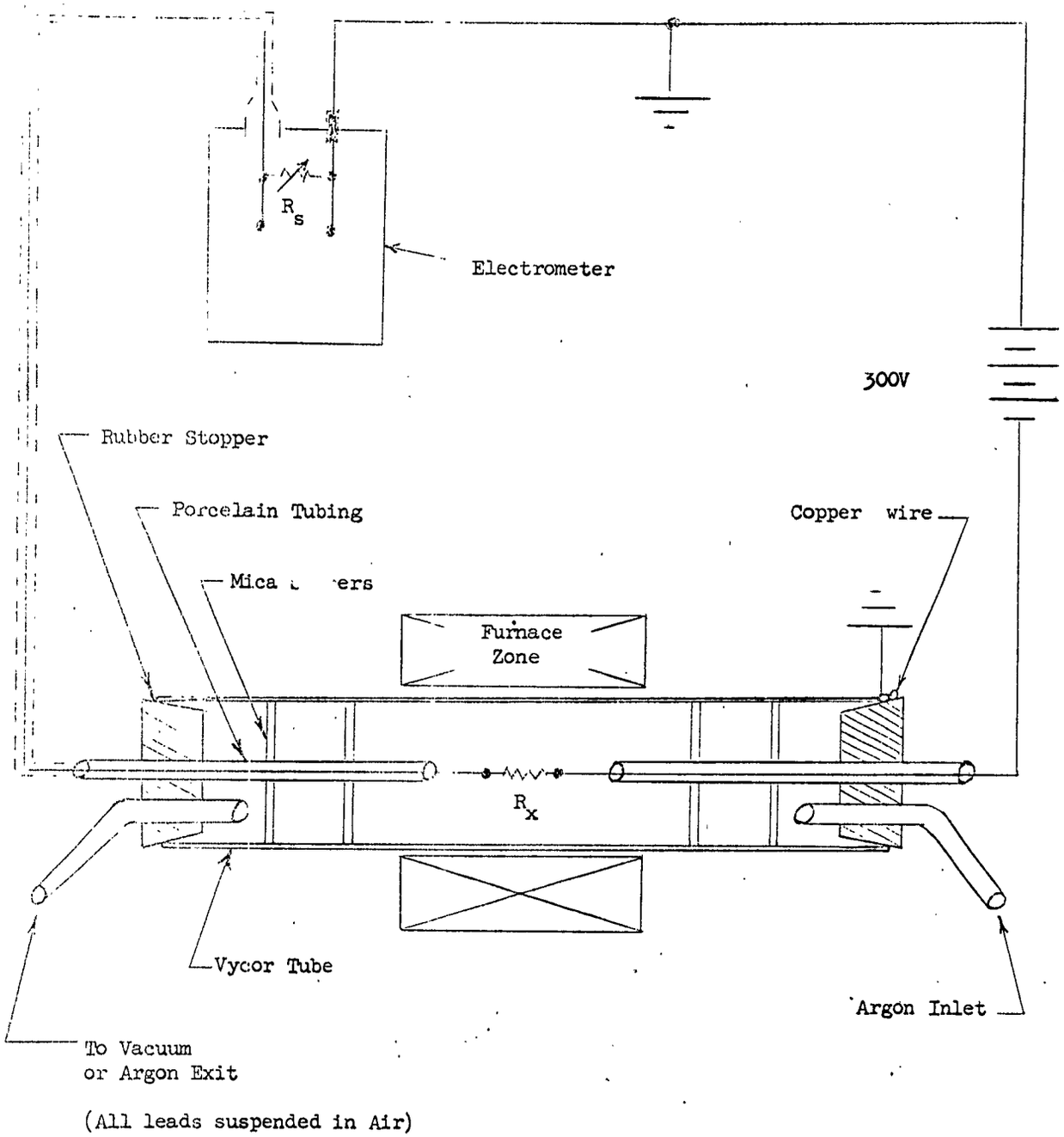


Figure 17

Diagram of Insulation Resistance Measuring Apparatus

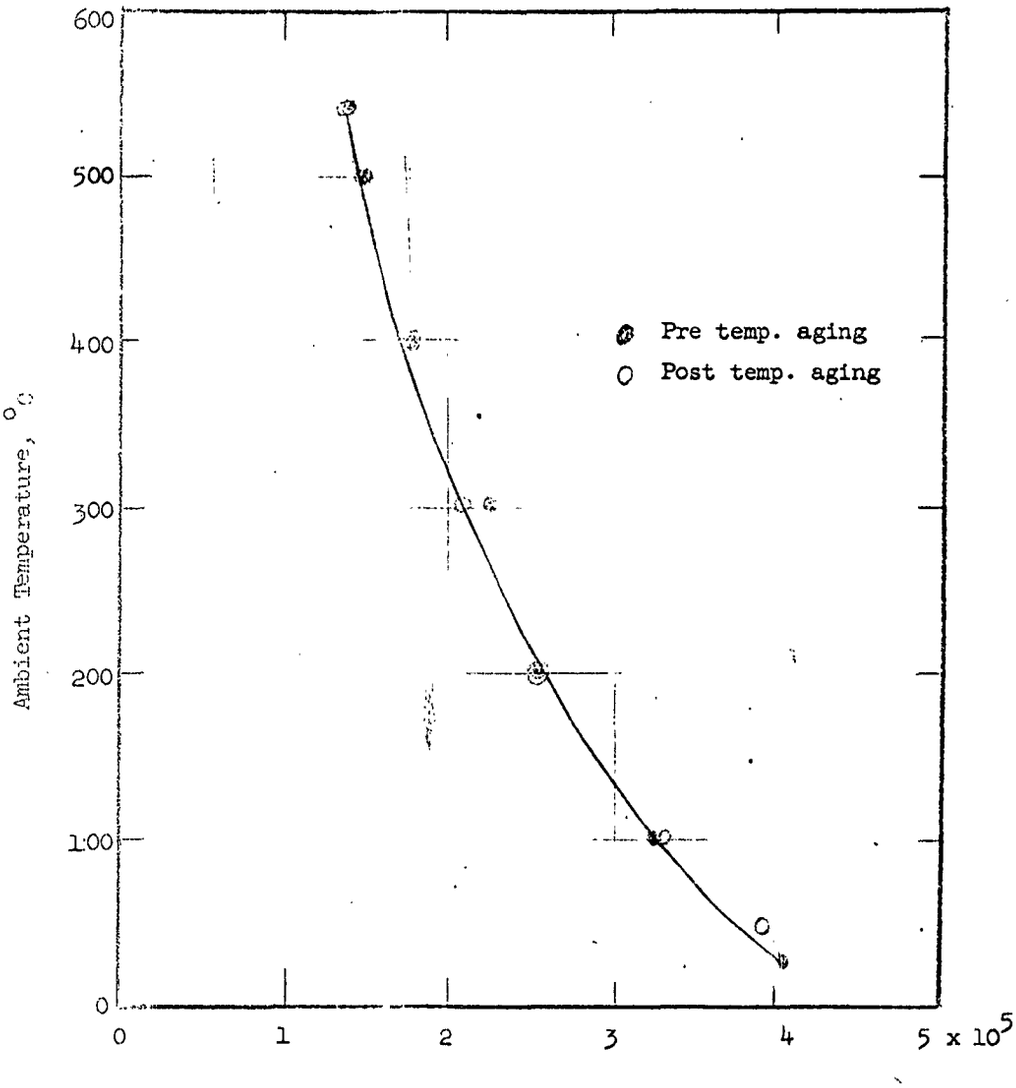


Figure 18. Pre and Post Aging Conductivity - Temperature Characteristics of "Oxalloy 28" in Argon.

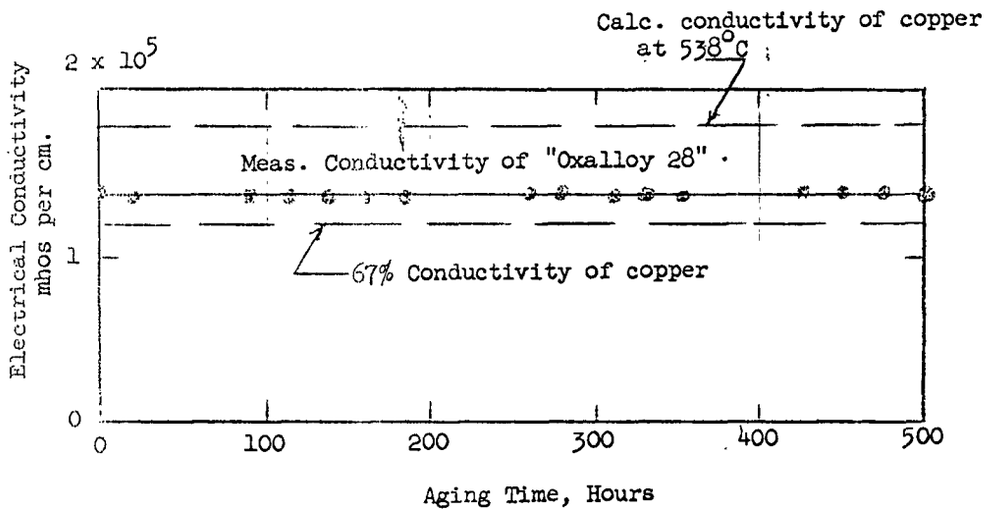


Figure 19. Temperature Aging - Conductivity Characteristic of "Oxalloy 28" in Argon at 538°C.

Figure -20-

Neg. No. CL-27050

Boron Nitride Deposit on Tungsten Wire

Figure -21-

Neg. No. CL-27190

Boron Nitride Deposits

Upper Left - Deposit on Graphite Rod
Lower Right - Deposit on Platinum Coil

Table I

Mercury Vapor Exposure Tests at 530°C

Identify	Sample	Time-Hrs.	Weight (grams) Before	After	Change
CH-7	Coram-Al_2O_3	260	2.8651	2.8649	-.0002
CH-7B	" "	"	2.0227	-	- Test not yet completed
CH-8	Thoria	"	.7672	.6681	-.0991
CH-9	ZrO - CaO	"	.7684	.7663	-.0021
CH-10	Hot Press MgO	"	5.8154	5.2504	-.565
CH-11	Flame Spray Al_2O_3	"	14.2048	14.2023	-.0025
CH-12	Pyroceram	"	.3383	.3383	-
CH-13	Sapphire Sphere	"	1.0445	1.0455	.001
CH-14	Beryllia	"	.6778	.6776	-.0002
CH-14B	Beryllia	"	2.3279	Test incomplete at this writing	
CH-15	MgO - Single Crystal	"	1.6414	1.6310	-.0104
CH-16	Aluminum Nitride	"	1.0626	1.0545	-.0081
CH-17B	Boron Nitride (Sintered)	"	.5716		
CH-18	Y-628 (e)	"	3.8928	Test incomplete at this time	
CH-19	Y-760 (e)	"	4.3932	Test incomplete at this time	
CH-20	Flame Spray Al_2O_3	"	2.0922	" " " " "	
CH-21	Sapphire Disc	"	.5423	" " " " "	
WH-3B	28% NiClad Cu (a)	340	1.2252	1.0065 .9333	
WH-5	Oxalloy (a)		1.5008	Test incomplete at this time	
WH-6	Cr plated Cu (b)	340	1.0795	" " " " "	
WH-6	Cr plated Cu (c)	"	3.0935	" " " " "	
WH-6	Cr plated Cu (d)	"	3.1539	" " " " "	
WH-7	Fe plated Cu (a)	"	.9936	" " " " "	

(a) Both ends beaded - hairpin shape
(b) Both ends beaded - hairpin shape
(c) One end plated - One end beaded
(d) Both ends beaded
(e) Strontium zirconate

Table II

Potassium Vapor Exposure Tests at 850°C

Identify	Sample	Time-Hrs.	Weight (grams) Before	After	Change
CK-1	Coors - Al_2O_3	125	1.1397	1.1482	.0085
CK-2	Lucalox - Al_2O_3	"	.3439	.3507	.0014
CK-3	Boron Phosphate - BPO_4	"	.4746	-	-
CK-4	Sauerisen No. 8	"	.6035	-	-
CK-6	Al_2O_3/Ta Seal	165	.3750	.3539	-.0211
CK-7	Coram, Al_2O_3	125	3.1059	3.1090	.0031
CK-8	Thoria	"	.8262	.8040	-.0222
CK-9	ZrO - CaO	96	1.8735	1.7638	-.1097
CK-10	Hot Pressed MgO	125	4.9116	4.9145	.0029
CK-11	Flame Sprayed Al_2O_3	"	14.3650	14.2764	-.0886
CK-12	Sapphire	"	1.0447	1.0457	.001
CK-13	Pyroceram	165	.3376	.3459	.008
CK-14	Beryllia	"	.6855	.6839	-.0016
CK-14B	"	"	2.1912	Test incomplete at this writing	
CK-15	Single Crystal MgO	"	1.2350	1.2349	-.0001
CK-16	Aluminum Nitride	"	.9602	-	-
CK-17	Boron Nitride	"	.6365	-	-
CK-18	Y-628	172	2.4631	Test incomplete at this writing	
CK-19	Y-760	"	4.7779	" " " " "	
CK-20	Flame Spray Al_2O_3	"	2.0797	" " " " "	
CK-17B	Boron Nitride $\cong$ Sintered	"	.5504	" " " " "	
WK-1	10% Ni plated Cu	"	.7924	.7905	.0019
WK-3	28% Ni clad Cu	"	1.2292	1.2290	-.0002
WK-5	28% Stainless clad Cu	"	1.2705	1.2677	-.0028

TABLE III

Properties of Potting Compounds

Sample	Filler	Binder	Green Strn.	Strn. after Exposure To 550°C	Strn. after Exposure To 875°C	Shrinkage Green	Shrinkage Fired
Sauereisen #9	Powder	Water	Fair	Poor	Poor	Low	ca 1%
Sauereisen #30	Powder	Water	Fair	Fair	Fair	Low	ca 3%
Sauereisen DW30	Powder	Water	Fair	Good	Fair	Low	ca 2.5
VG 107	Silicates	Phosphate	Good	Excellent	Very good	ca 2%	ca 3%
W 839	Silicates	Phosphate	Good	Very good	Excellent	Low	Low
S 7-63-1	Alumina	Collodial Zirconia	Poor	Fair	Good	High	--
S-7-63-2	Alumina	Mag. Metholate	Very poor	None	None	High	--
*S-7-63-3	Magnesia	Collodial Zirconia	Fair	Fair	Fair	High	--
S-7-63-3	Magnesia	Mag. Metholate	Poor	None	None	High	--

*Formed a paste on mixing; additional collodial zirconia solution did not fluidize the mixture.