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Alkali Metal Resistant Wire

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FOREWORD

This preliminary report is submitted by the Aerospace Electrical Division, Westinghouse Electric Corporation, Lima, Ohio, on Air Force Contract AF33(657)10701, Project No. 8128, Task No. 8128-06, "Development of High Temperature Alkali Metal Resistant Insulated Wire". The contract is administered by the Air Force Aero-Propulsion Laboratory, Research and Technology 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

A ceramic coated conductor system was developed that was unaffected by 172 hours exposure to K (potassium) vapor at 850 C. This system was Metco 201 zirconia, plasma sprayed on nickel aluminide coated Nickel clad Silver AWG 8 (Sylvania) wire. This system, however, is not suitable for electrical operation at 850 C since the resistance of the zirconia coating drops to about 5 ohms at 600 C. Overcoating the zirconia with aluminum nitride by a vapor plating technique results in a resistance at 850 C in argon for the multicoat of 1.8 x 10^4 ohms. The aluminum nitride overcoated zirconia is unaffected by 172 hours exposure. Post exposure electrical resistance measurements of the coating were not completed. However, no significant decrease in resistance due to potassium vapor is anticipated. A number of high purity insulators were found to be resistant to potassium vapor at 850 C. These were alumina, magnesia, and strontium zirconate. A primary problem with plasma spray coatings of these materials is loss of adhesion in the potassium vapor even when a nickel aluminide undercoat is used. Pre- and post-potassium vapor (850 C) exposure resistance data on many materials was obtained; however, the electrical leakage resistance of the materials, while exposed to the metal vapors could not be properly meausred due to lack of a satisfactory electrical test capsule. Data obtained on lead in insulators of test capsules indicates a decrease in surface resistivity, however, the lowered resistance of these insulators (10^4 ohms) is still in a useful range. Statorette adherence tests show several insulated conductors will withstand vibration, shock and acceleration conditions.

Two insulated conductors were exposed to a nuclear environment of 10^{19} thermal neutrons and 10^8 rads gamma. The insulation resistance decreased in both insulation coatings.

A statorette coil of nickel clad silver wire was partially insulated with nickel aluminide, zirconia and alumina (98%) coating. The remaining portions of the conductor were coated with nickel aluminide and very high purity alumina (99.9%). The high purity alumina remained on the conductor after 172 hours, while the other insulating coating of zirconia (99.9%), alumina (98%) cracked and came off.

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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 alternator 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 was 10,000 hours. The resistance of the conductor at test temperature during its life was not to exceed 150% of the copper standard at 850 C. The room temperature tensile strength of the conductor was to be in excess of 30,000 psi. The initial purity of the potassium used in the exposure tests was 99.7%.

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

The final evaluation of the insulated wire was done in statorettes. The insulated conductor was placed in statorettes to investigate winding techniques. While in the statorette, the insulation system was subjected to metal vapors, temperature, thermal shock, nuclear radiation, vibration, mechanical shock, humidity and acceleration.

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II. Summary of Work Performed and Major Results

1. Ninety-eight specimens were exposed to K potassium vapor at 850 C and thirty-five specimens were exposed to Hg mercury vapor at 538 C. The specimens included insulators, electrical conductors, brazing alloys, glasses, sealed joints and insulation coated strips, rods and wires. A stainless steel Swagelok on a stainless steel tube was the only joint made at room temperature that held leak tight at 850 C.

2. Metallurgical examination of conductor samples exposed to metal vapors show no significant attack on the Oxalloy 28 (stainless steel clad copper conductor) 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.

   The Ni clad Ag wire supplied by Sylvania was unaffected by 170 hours exposure to K vapor at 850 C. The ends of the wire specimen were sealed by a 7 mil Ni electroplate.

   Oxalloy 28 was selected as the conductor for the mercury vapor service and Inconel clad and Ni clad silver as the conductors for the potassium vapor service.

3. 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 formed and the alumina coatings contained some aluminum metal layers.

4. 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.

5. Initial results from attempts to densify porous coating 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 across a thermal gradient distance of 15 cm in a dry HC1 hydrogen chloride (10 atm.) atmosphere. Work on the approach was terminated prior to completion of the investigation because conclusive results were not obtained.

6. The BN coating formed by thermal decomposition of trichloroborozole was found to provide some protection to surfaces

exposed to potassium vapor at 850 C for 172 hours. The coating on wire specimens powdered somewhat during the metal vapor exposure, but the film remaining was nonconducting. Infrared spectra data on the coatings indicate them to be BN, but of varying crystallinity. Only films formed at temperatures of 1400 C or higher had the desired hexagonal structure. Also, the coatings tended to hydrolyze and give off an ammonia odor while standing at room temperature in air.

7. Powdered alumina in collodial zirconia produced adherent, uniform coatings on stainless steel, Inconel and nickel substrates when fired at 1000 C. However, the coatings disintegrated during the potassium vapor exposures at 850 C.

8. Al N (aluminum nitride) coatings were successfully formed at 800 C on Mo (molybdenum) and W (tungsten) rods and on Ni (nickel) clad Ag (silver) wire precoated with zirconia (Metco 201). The Al N overcoated zirconia was not affected by 172 hours exposure to potassium vapor at 850 C. The Al N coatings would not adhere to Inconel, nickel or stainless steel substrates directly.

9. Plasma sprayed zirconia on Ni Al (nickel aluminide) (Metco 404) coated Ni clad Ag wire was unaffected by a 172 hour exposure to potassium vapor at 850 C. Uniform adherent coatings of various oxides were successfully applied to preformed coils of Ni clad and Inconel clad silver wire. The coatings applied were alumina, magnesia, zirconia and strontium zirconate.

10. Three brazing alloys that wet sapphire were found that had fair resistance to attack by K vapor at 850 C. These alloys were 95% Zr-5% Be, 68% Ti-28% V-4% Be, and 72% Ti-28% Ni. A number of leak tight electrical test capsule units were prepared using the 95% Zr-5% Be alloy to seal the OD of a sapphire disk to the ID of a tantalum tube. A Ta wire penetrating the center of the sapphire disk was sealed with the same alloy. All the units eventually failed on repeated thermal cycling due to cracking of the sapphire at the lead wire. Stainless steel tubes were brazed to the tantalum tubes using Nicrobraze 30 and 130 to form leak tight joints that were suitable for use with the stainless steel Swagelok units.

11. A Lucalox tube to Niobium flat plate joint made with an alumina-calcia glass was not affected by 172 hours exposure to K vapor at 850 C.

12. The average conductivity measured on chrome plated and iron plated OFHC copper wire aged in argon at 540 C for 500 hours was 97% and 87% respectively of that calculated for copper at 540 C. The aging resulted in a permanent decrease in the conductivity of the iron plated OFHC copper wire.

13. Two specimens of Oxalloy 28 wire were aged in argon at 850 C for 500 hours. Conductivity of the two samples dropped below the minimum value (67% of Cu standard) after 400 hours and 100 hours respectively.

14. Pre-exposure of Oxalloy 28 to mercury vapor at 540 C for 360 hours did not result in any significant change in conductivity of the wire during 500 hours aging at 540 C in argon.

15. The electrical conductivity of Sylvania's nickel clad (20%) silver wire remained a constant 89% of the calculated value for copper during a 500 hours aging at 850 C in argon.

16. The volume resistivity at 540 C was determined for seven insulators, four of which had been pre-exposed to mercury vapor at 540 C for 260 hours. The resistance of beryllia decreased from 10^{10} to 10^4 ohm-inches. The resistivity of strontium zirconate after vapor exposure was 1.4×10^7 ohm-inches at 540 C.

17. The volume resistivity at 850 C was determined for six insulators, three of which had been pre-exposed to potassium vapor at 850 C for 165 hours. Hot pressed magnesia decreased from 2.5×10^6 to 7.8×10^3 ohm-inches. The resistivity of strontium zirconate after vapor exposure was 6.5×10^4 ohm-inches at 850 C.

18. Electrical leakage resistance in argon at 850 C measured on an experimental lead in assembly was 9.7×10^7 ohms. The assembly consisted of a 1/2" dia. Lucalox disk brazed with 95% Zr-5 Be into the ID of a tantalum tube and having a molybdenum lead wire sealed in a hole through the Lucalox disk of the same alloy.

19. Electrical volume resistivity and leakage resistance at 850 C in argon were determined for a stainless steel clad, magnesia powder insulated OFHC copper conductor supplied by Advanced Technology Laboratory. The measured values were 1.4×10^8 ohm-inches and 9.3×10^6 ohms per inch respectively.

20. Electric leakage resistance measurements were made on the five mercury vapor filled capsules incorporating the commercial lead in assemblies. All units developed leaks prior to attaining a temperature of 540 C.

21. A test capsule consisting of a tantalum tube and sapphire disk was charged with potassium and the electrical leakage resistance of the sapphire was measured at temperatures to 850 C. At 850 C the value was 9.1×10^4 ohms as compared to 5.7×10^7 ohms when the capsule contained 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.

22. The electrical leakage resistance of a plasma sprayed zirconia coating (Metco 201) on a nickel rod was measured at temperatures up to 850 C. At 600 C, the resistance had decreased to 5 ohms.

23. The electrical leakage resistance in argon was determined on a capsule formed by sealing Nb end caps to a Lucalox tube with an alumina-calcia glass. A value of 2.2×10^7 ohms was measured at 850 C.

24. The electrical leakage resistance in argon of an Al N coating on a Mo rod was 4.0×10^5 ohm at 850 C. The resistance under the same conditions of an Al N overcoated zirconia (Metco 201) coating on Ni Al coated Ni clad Ag wire was 1.8×10^4 ohm.

25. Two insulated test coils formed from Inconel clad Ag wire were sent to Brookhaven National Laboratories for radiation exposure. One coil was insulated with plasma sprayed strontium zirconate and the other had a plasma sprayed alumina (Metco 105) over plasma sprayed zirconia (Metco 201).

26. A preformed coil of nickel clad silver wire, conductor size No. 8 B & S, was plasma-arc coated with nickel aluminide, zirconia (99%) and alumina (98%).

27. A second preformed coil of nickel clad silver wire, No. 8 size, was plasma-arc coated with molybdenum, zirconia and alumina.

28. These insulated conductors described in 26 and 27 above were subjected to vibration acceleration and shock (50g) tests. The

insulating ceramic coating remained intact. A (100%) humidity exposure of ten days caused the leakage current to increase from a value of 2.8 micro amperes to 96 micro amperes. A voltage of 500 VAC was used for these leakage tests.

29. Two samples of insulated Inconel clad silver wire with different ceramic coatings were exposed to nuclear pile radiation. The total radiation dose received was 10^{19} thermal neutrons and 10^{8} gamma. The electrical resistance of both coatings decreased and 50% of the zirconia, alumina over molybdenum coating came off the Inconel clad silver conductor.

30. A statorette coil of nickel clad silver wire was partially insulated with nickel aluminide, zirconia and alumina (98%) coating. The remaining portions of the conductor were coated with nickel aluminide and very high purity alumina (99.9%). Electrical resistance measurements of this conductor in 850 C potassium vapor was on the order of 10^{4} ohms, however failure of the electrical terminal seals terminated the test. Post examination of this coil showed extensive attack on the zirconia, alumina portion of the coating but the high purity alumina resisted attack by the 850 C potassium vapor.

31. The mercury vapor exposure of the statorette coil was not done as no satisfactory terminal seal was available. Test results on 538 mercury vapor corrosive effects indicate very little if any, corrosion of ceramic coatings.

III. Fundamental Considerations of Corrosion Resistance

3.1 Insulation

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 Micro Structure, Micro Fissures, 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 micro fissures on bending, allowing penetration of the metal vapors. When crystalline materials are applied to substrates, micro fissures can also develop during thermal cycling due to excessive stresses, resulting from unequal coefficients of thermal expansion of the two materials.

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 cooefficient of thermal expansion of the conductors. Since metal vapor resistance, insulation resistance and conductor conductivity limits the availability of usable oxides and conductors, ideal conditions do not prevail. The materials considered for the insulating coatings are 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 from contract 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 rate between the conductor and cladding at elevated temperatures. Sufficient data is available on the liquid metal resistance of metals to select candidate cladding materials with some assurance of good performance. (2)

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

4.1 Metal Vapor Exposure, Mercury and Potassium

4.1.1 Test Capsules Design and Fabrication

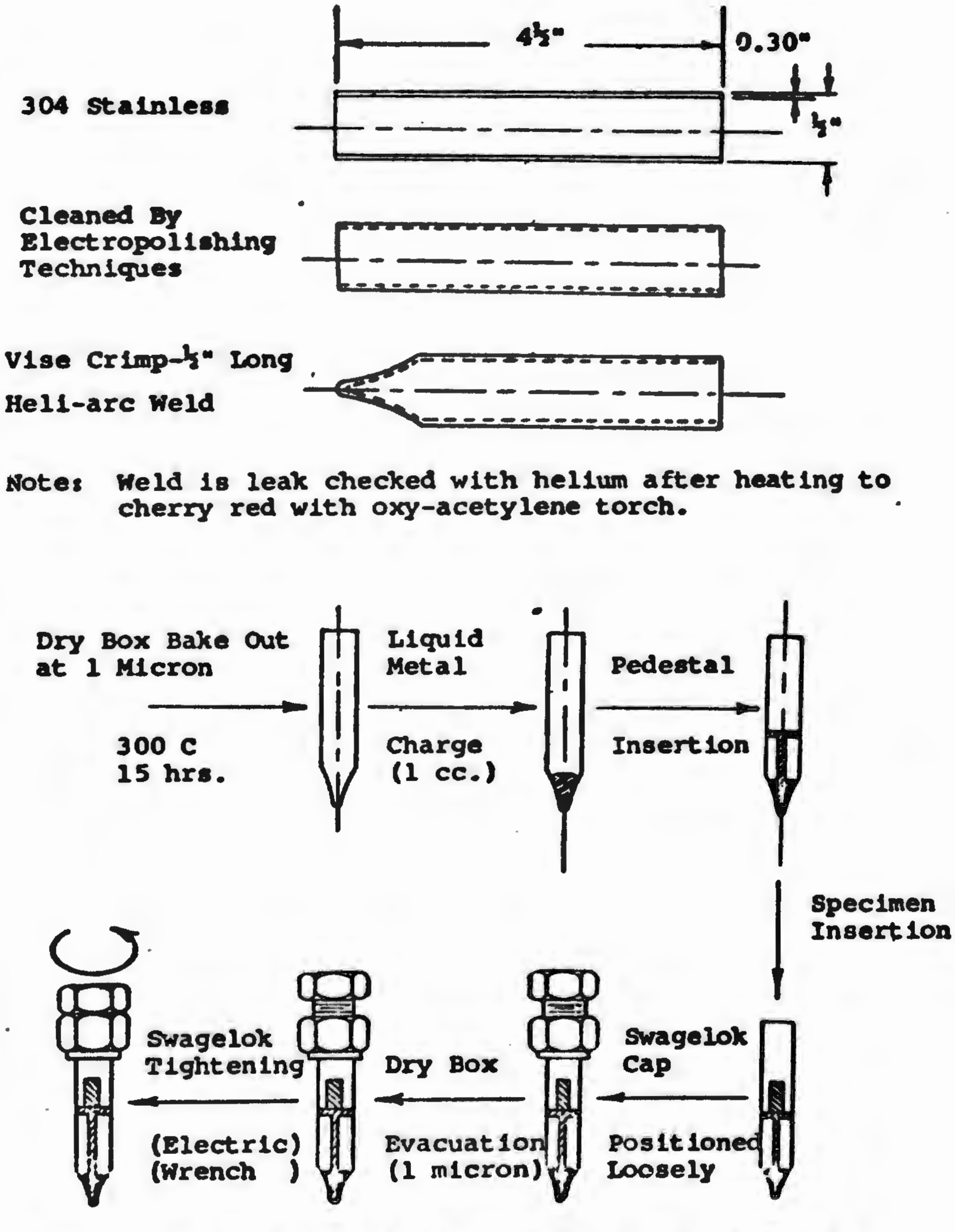
Figure 1 contains a detailed drawing of the corrosion test capsules and a flow diagram illustrating the techniques used to clean and fabricate them. The majority of the capsules were 1/2" O. D. .025" wall thickness stainless steel, although a number of 1" O. D. capsules were sealed during the program. One end is sealed by a crimping/welding operation while the other end, after capsule filling, is sealed in a vacuum with the use of a 1/2" Swagelok cap (Cat. #810-C-316). Early plans to seal the capsule by crimping were not successful. It was found the crimped 304 stainless steel tube ends did not provide a vacuum tight seal.

A large dry box capable of evacuation to 1×10^{-3} torr was procured and installed. Dry argon was passed into the dry box from a NaK bubbler operating at 600 F. It was also equipped with an electric wrench capable of tightening Swagelok fittings of 1" maximum diameter remotely under a high vacuum environment. The electric impact wrench was eventually discarded in favor of a vertical shaft passing through the top of the dry box and sealed to it through a four unit rubber o-ring seal. By equipping this shaft with the appropriate socket and bar arrangement, Swagelcks could then be sealed manually. The above modification was necessary because of frequent failures experienced with the electric wrench and excessive outgassing during operation due to armature and stator winding deterioration.

4.1.2 Sample Exposure

The specimens of material were 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 were only available in specific forms.

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. The listing of exposed specimens with weight loss data and remarks are contained in Tables 1 and 2.



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.

Figure 1 - Cleaning and sealing technique for corrosion test capsules

TABLE 1
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Ck-1	Coors-Al_2O_3	125	1.1397	1.1482	.0085	Purple discoloration
Ck-2	Lucalox-Al_2O_3	125	.3439	.3507	.0014	No change
Ck-3	Boron Phosphate-BPO_4	125	.4746	-----	-----	Sample disintegrated
Ck-4	Saureisen #8	125	.6035	-----	-----	Sample disintegrated
Ck-6	Al_2O_3/Ta Seal	165	.3750	.3539	-.0211	Seal separated
Ck-7	Coram, Al_2O_3	125	3.1059	3.1090	+.0031	No change
Ck-8	Thoria	125	.8262	.8040	-.0222	Light Purple-cracked
Ck-9	Zro-CaO	96	1.8735	1.7638	-.1097	Surface dark
Ck-10	Hot pressed MgO	125	4.9116	4.9145	.0029	Deep purple
Ck-11	Flame Sprayed Al_2O_3	125	14.3650	14.2764	-.0886	Coating lifted
Ck-12	Sapphire	125	1.0447	1.0457	.001	Slight surface etch
Ck-13	Pyroceram	165	.3376	.3459	.008	Surface black
Ck-14	Beryllia	165	.6855	.6839	-.0016	No change
Ck-14B	Beryllia	165	2.1912	2.1996	+.0084	No change

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Ck-15	Single Crystal MgO	165	1.2350	1.2349	-.0001	No change
Ck-16	Aluminum Nitride	165	.9602	-----	-----	Metal initially soft
Ck-17	Boron Nitride	165	.6365	-----	-----	Metal initially soft
Ck-18	Y-628 Strontium Zirconate	172	2.4631	2.4641	+.001	Light purple
Ck-19	Y-760 Strontium Zirconate	172	4.7779	4.7673	-.0106	Light purple
Ck-20	Flame Spray Al_2O_3	172	2.0797	-----	-----	Coating lifted
Ck-17B	Boron Nitride (BN) Sintered	172	.5504	-----	-----	Sample lost-capsule leak
Ck-21	Sapphire disc		.5423	-----	-----	Sample lost due to capsule corrosion
Ck-22	Ni coated BeO		.1698	-----	-----	Sample lost due to capsule corrosion
Ck-23	BN coated graphite		9.2922	-----	-----	Graphite cracked into pieces
Ck-24	BN film-1000C anneal		-----	-----	-----	Film intact

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Ck-25	BN film-1000C anneal		-----	-----	-----	Film intact
Ck-26	BN film-No anneal		-----	-----	-----	Film intact
Ck-27	RC-28-2AlN foam graphite		.0779	.0635	.0144	No apparent change
Ck-28	RC-35-1 AlN on graphite		2.4578	-----	-----	Sample disintegrated
Ck-29	R07-1 Al_2O_3/AlN		4.1414	3.6396	.5018	Coating lifted
Sk-2	Tube to Tube ceramic seal		10.0242	-----	-----	Sample lost due to heavy capsule corrosion
Sk-3	Ceramaseal		6.3993	-----	-----	Sample disintegrated
Sk-4	Stainless/Lucalox (95 Zr-5 Be)		.9985	-----	-----	Sample lost due to heavy capsule corrosion
Sk-5	Kovar/Sapphire (95 Zr-5 Be)		-----	-----	-----	Sample lost due to heavy capsule corrosion
Sk-6	Kovar/Lucalox (95 Zr-5 Be)		.5433	.5481	+.0048	Seal came apart

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Sk-7	St. Steel/Lucalox (95 Zr-5 Be)		.6796	.6801	+.0005	Seal came apart
Sk-8	St. Steel/Lucalox (95 Zr-5 Be)		.6561	.6568	+.0007	Seal intact
Sk-9	Kovar/Lucalox (95 Zr-5 Be)		.5380	.5394	.0014	Seal intact
Sk-10	Ta/Lucalox (95 Zr-5 Be)		.9558	.9542	.0016	Seal came apart
Sk-11	Ta/Lucalox (95 Zr-5 Be)		.8566	.8572	.0006	Seal came apart
Wk-1	10% Ni plated Cu		.7924	.7905	.0019	
Wk-3	28% Ni clad Cu		1.2292	1.2290	-.0002	No apparent change
Wk-5	28% Stainless clad Cu		1.2705	1.2677	-.0028	No apparent change
Wk-8	Anodized Ta rod		35.3413	-----	-----	Sample lost - heavy capsule corrosion
Wk-9	Anodized Nb rod		13.4054	-----	-----	Sample lost - heavy capsule corrosion
Wk-10	Bn coated Oxalloy		3.9993	-----	-----	Sample unchanged
Bk-1	45 Ti-40 Zr-15 Fe		.1191	.1205	.0014	Sample darkened

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Bk-2	80 Zr-17 Fe-3 Be		.1747	.1812	.0065	Sample darkened rough surface
Bk-3	48 Zr-48 Ti-4 Be (Ta/Lucalox)		.7953	.7884	-.0069	Sample broke apart
Bk-4	75 Zr-19 Cb-6 Be (Ta/Lucalox)		.7408	.7408	-----	Sample broke apart
Bk-5	62 Ti-26 Fe-8 Mo-4 Zr (Ta/Lucalox)		.6447	.5110	-.1337	Sample broke apart
Bk-6	63 Ti-27 Fe-10 V (Ta/Lucalox)		.7963	.6974	-.0989	Sample intact - capsule leak
Bk-7	63 Ti-27 Fe-10 Mo (Ta/Lucalox)		.5806	.5784	-.0022	Sample intact
Bk-8	68 Ti-28 V-4 Be (Ta/Lucalox)		.5615	.5629	+.0014	Sample intact
Bk-9	Nicrobraze 130-Vacuum heated		1.1684	1.1678	-.0006	Slightly discolored
Bk-10	Nicrobraze 130-Argon heated		.9790	.9789	-.0001	Slightly discolored
Bk-11	28 Ni-72 Ti		.6326	.6289	-.0037	Slightly discolored
Bk-12	62.5 Ti-37.5 Ni		.4429	.4488	+.0059	Slightly discolored

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Bk-13	Lucalox/Tantalum joint		.3299	.3280	-.0019	No apparent change
Pk-1	S7-63-1		2.0084	-----	-----	Disintegrated
Pk-2	S-30		1.8062	-----	-----	Disintegrated
Pk-3	Lig-107		1.5521	-----	-----	Disintegrated
Pk-4	S-9		2.0909	-----	-----	Disintegrated
Pk-5	W-839		2.9806	-----	-----	Disintegrated
Pk-6	Alumina-101		14.1272	14.0544	-.0728	Film badly attacked
Pk-7	ZrO-Hafnium free XP-115		14.2052	14.2121	+.0069	Sample film intact - purple
Pk-8	ZrO-201		14.4333	14.2469	-.1864	Sample film intact - purple
Pk-9	15-A-7-SS		2.5685	2.5097	-.0588	Coating disintegrated badly
Pk-10	Alumina 105		14.3829	14.3878	+.0049	Film lifted
Pk-11	Silica free Al_2O_3		.8248	.8267	.0019	Turned gray-white powder leaked out

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Bk-14	Lucalox/Ta-Ti/Ni braze	170	.8928	.8884	-.0037	Sample broke apart
Wk-11	Ni clad Ag-ends Ni plated	170	6.9429	6.9334	-.0095	No apparent change
Wk-12	Ni clad Ag+Metco 1115 ZrO	170	4.4192	-----	-----	Sample lifted
Wk-13	Ni clad Ag+Metco 105 Al_2O_3	170	4.9675	-----	-----	Sample lifted
Wk-14	Ni clad Ag+Metco 201 ZrO	170	4.6750	-----	-----	Sample lifted
Wk-15	Same as Wk-12; uncoated end	170	4.5690	-----	-----	Sample lifted
Wk-16	Same as Wk-13; uncoated end	170	4.7636	-----	-----	Sample lifted
Wk-17	Same as Wk-14; uncoated end	170	4.6193	-----	-----	Sample lifted
Wk-18	Ni clad Ag-sprayed with Ni Al	170	5.2995	1.5691	-3.7304	Coating intact; Ag core
	+ZrO; Metco 201 with AlN	170				Attacked thru welded end

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Wk-19	Ni clad Ag-Lima sample		6.5888	6.4004	-0.1884	Coating lifted*
Wk-21	Ni rod + Metco 1115 ZrO coated end		4.7724	4.6854	-.0870	Coating lifted (capsule leaked)*
Wk-24	Ni rod + Metco 1115 ZrO uncoated end		4.8950	4.8336	-.0614	Coating lifted (capsule leaked)*
Wk-22	Ni rod + Metco 201 ZrO		4.6831	4.5987	-.0844	Coating lifted*
Wk-25	Ni rod + Metco 201 Uncoated end		3.6708	3.6439	-.0469	Coating lifted*
Wk-23	Ni clad Ag		4.8358	4.8349	-.0009	Light purple hue
Ck-31	Strontium Zirconate on NiAl coated Inconel		14.7999	14.8700	+.0701	Film lifted from NiAl layer
Ck-32	Cerac-4 sintered AlN		.6735	.6638	-.0097	No apparent change
Bk-26	Lucalox/Nb joint using		5.5246	5.5030	-.0216*	No apparent change wt. loss during post exposure bake
Ck-33	Strontium Zirconate plasma sprayed on NiAl coated Inconel strip		14.3980	-----	-----	Coating lifted - adhesion failure

*Samples may have been damaged on removal from capsule.

TABLE 1 (Cont.)
POTASSIUM VAPOR EXPOSURE TESTS AT 850 C

Identity	Sample	Time Hrs.	Before	After	Change	
Sk-12	Metallized Alote 610 OFHC copper brazed to a nickel then Ni plated		4.1415	-----	-----	Sample inpure after test
Sk-13	Lucalox/Ta joint with Ti-Ni alloy test capsule unit		3.2127	2.9719	-.2408	Purple deposit on Lucalox joint no longer leak tight

TABLE 2
MERCURY VAPOR EXPOSURE TESTS AT 540 C

Identity	Sample	Time Hrs.	Wt. Inform. - Grams Before	After	Change	Comments
Ch-1	Al_2O_3-AD 99	260	.8712	.8719	+.0007	Black surface
Ch-2	Lucalox	260	.5360	.5363	+.0003	Black surface
Ch-3	BPO_4	260	1.2328	1.2334	+.0006	Black surface
Ch-4	Saureisen #8	260	.6645	.6636	-.0009	Grey surface
Ch-5	Lucalox/Ta	260	.2371	.2366	-.0004	Ceramic separated from Ta
Ch-6	Al_2O_3/Ta	260	.3741	.3747	+.0006	No visible change in seal. Al_2O_3 darkened
Ch-7B	Al_2O_3-Coran	260	2.0227	2.0146	-.0081	No apparent change
Ch-14B	Beryllia	260	2.3279	2.3277	.0002	No apparent change
Ch-18	Y-628 Strontium Zirconate	260	3.8928	3.8263	-.0065	No apparent change slight chip
Ch-19	Y-760 Strontium Zirconate	260	4.3932	4.3527	-.0405	Surface pocked
Ch-20	Al_2O_3-Flame sprayed	260	2.0922	2.0918	-.0004	Surface darkened
Ch-22	Ni coated BeO	260	.1545	.1530	-.0015	Surface black

TABLE 2 (Cont.)
MERCURY VAPOR EXPOSURE TESTS AT 540 C

Identity	Sample	Time Hrs.	Wt. Inform. - Grams Before	After	Change	Comments
Wh-1	Ni plated Cu-10% Ni (10% Ni)	340	.8084	-----	-----	No sample remaining
Wh-2	Ni plated Cu-10T Ni (10% Ni)	340	.8143	-----	-----	No sample remaining
Wh-3	Ni clad Cu-28% Ni	340	1.2136	1.0514	-.1622	Portions of Cu core missing holes in Ni clad
Wh-4	Ni clad Cu-28% Ni	340	1.2162	1.1192	-.0970	Same as Wh-3
Wh-5	Oxalloy-28% St. St. Clad	340	1.2245	1.1410	-.0835	Stainless blackened
Wh-5	Oxalloy-28% St. St. Clad	340	1.5008	1.4780	-.0228	Surface black
Wh-6	Cr plated Cu-both ends welded	340	1.0795	-----	-----	Cu core heavily attacked
Wh-6	Cr plated Cu-one end plated-one weld	340	3.0935	-----	-----	Sample disintegrated
Wh-7	Fe plated Cu	340	.9936	-----	-----	Sample disintegrated
Wh-8	Anodized Ta	340	35.6448	35.6462	+.002	Surface conductive after test

TABLE 2 (Cont.)
MERCURY VAPOR EXPOSURE TESTS AT 540 C

Identity	Sample	Time Hrs.	Wt. Inform. - Grams Before	After	Change	Comments
Wh-9	Anodized Nb	340	13.3753	13.3759	+.0006	Surface conductive after test
Sh-2	Ceramic-to-Metal seal	260	12.5337	-----	-----	Brazing alloy heavily attacked
Sh-3	Ceramaseal	260	6.7223	6.4121	-.3102	Brazing alloy attacked
Sh-5	Ceramaseal/SS tube-series 801		---------------For electrical tests---------------			
Sh-6	Ceramaseal/SS tube-series 805		---------------For electrical tests---------------			
Sh-7	Ceramaseal/SS tube-series 801		---------------For electrical tests---------------			
Bh-6	63 Ti-27 Fe-10 V	100	.5452	.5454	+.0002	Sample darkened slightly
Bh-8	68 Ti-28 V-4 Be	100	.1118	.1104	-.0014	Sample darkened slightly
Bh-12	62.5 Ti-37.5 Ni	100	.1303	.1303	-----	Sample darkened slightly

TABLE 2 (Cont.)
MERCURY VAPOR EXPOSURE TESTS AT 540 C

Identity	Sample	Time Hrs.	Wt. Inform. - Grams			Comments
			Before	After	Change	
Bh-13	62.5 Ti-37.5 Ni (Lucalox/Ta joint)	100	.8486	.8489	+.0003	Sample darkened slightly
Bh-14	95 Zr-5 Be	100	.0846	.0703	-.0143	Sample darkened slightly
Bh-15	71.5 Ti-28.5 Ni	100	.1327	.1300	-.0027	Sample darkened slightly

4.1.3 Sample Removal and Cleaning

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 following this treatment. The cleaning procedure for preparing specimens for examination after exposure to mercury is as follows: rather than subject the sample to a dilute nitric acid dip, it was 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.

It can be seen from Table I that data on ten potassium vapor tests were lost due to heavy corrosion of the capsules. Figures 2 and 3 show one set of such capsules on removal from the aging oven. It will be noted in Figure 3 that the bottom half of the capsules is severely attacked. It is theorized that one of the capsules leaked due to a defective weld or Swagelok fitting, and the leaking potassium vapor oxidized and settled into the 1" O. D. receptacles holding the remaining capsules. The higher corrosive oxide or hydroxide then attacked the type 304 stainless steel resulting in eventual punctures of all tubes mounted in this way. The fact that two capsules standing free along side of the holding block suffered no attack and remained tight supports this theory.

4.1.4 Cover Gas Purification Facilities

The argon used as a cover gas during capsule charging was purified in a bubbler using NaK 78 at 600 F. The resulting O_2, N_2 and H_2O content is below the sensitivity of our mass spectrometer ($<$ 2 ppm). The potassium used in the preliminary tests is obtained from MSA Research Corp. and has an oxide content of $<$ 50 ppm. The mercury metal as obtained from the supplier is about 5 ppm contaminated.

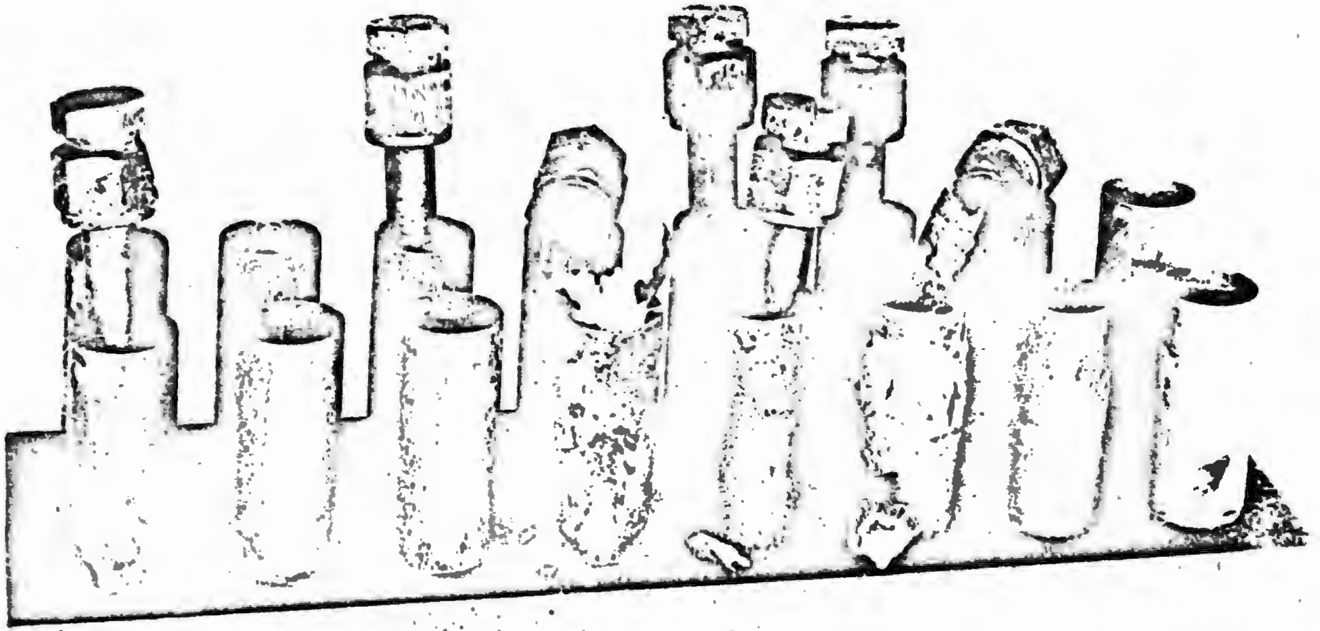


Figure 2. Potassium Exposure Capsule Holder Immediately on Removal From Aging Oven

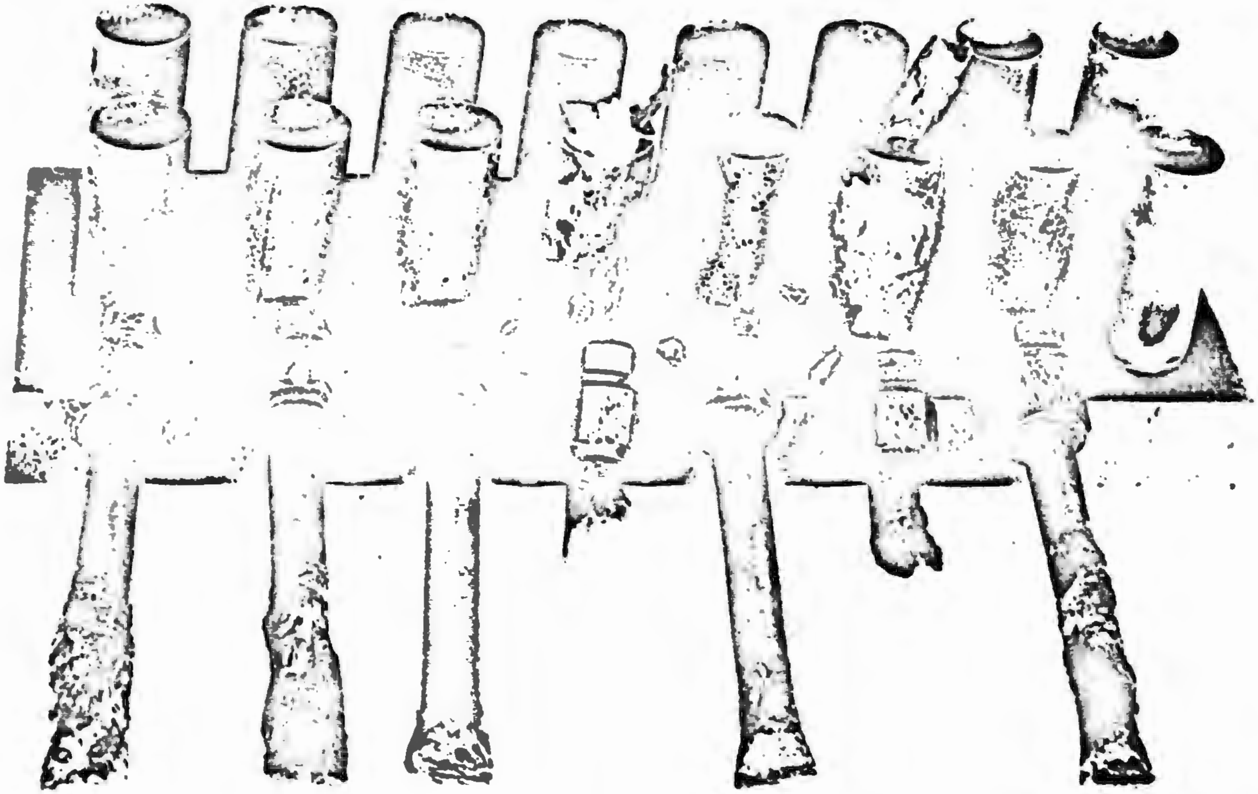


Figure 3. Potassium Exposure Capsules Removed From Holder

4.1.5 Sealing of Tantalum Test Capsules

Attempts to obtain a tantalum tube to stainless Swagelok joint that remains vacuum tight up to 540 C, were unsuccessful. A stainless liner pressed into the tantalum tube before sealing increased the systems upper temperature capability to about 400 C. Since a number of promising metal to ceramic seals use tantalum, a Swagelok fabricated from this refractory metal was obtained. It was believed that a tantalum tube to tantalum Swagelok would eliminate the 400 C leak problem experienced when materials of dissimilar thermal expansion coefficients were used. It was found, however, that this was not the case. The Ta/Ta joint again began leaking at a temperature of 400 C indicating that such a system is not practical as a vacuum tight joint above this temperature.

4.2 Electrical Conductors

4.2.1 Candidate Selection

The available information on electrical conductors suitable for extended service at 850 C and 538 C was reviewed. Even though copper might present possible grain growth problems at 850 C as reported by Anaconda in their work on contract AF33(616)7473, the great limitation imposed on coating methods and materials by silver's low melting point (960 C) justified some consideration of copper cores for the potassium vapor environment. The grain growth affects only the ultimate tensile strength of the conductor and would only affect the electrical properties if the grains slip one on the other to effect a reduction of cross section of area on the wire at isolated points. The use of refractory metal cladding could prevent slipping at the grain boundaries. The larger diameter of the wire in this program (#8 or #10 versus the #18 and #30 used by Anaconda) would provide a finer initial grain size due to fewer annealing treatments. In addition to OFHC copper, cores of zirconium copper and dispersion hardened (thoria, beryllia) copper were considered as means of preventing grain growth.

Inquiries placed with Anaconda revealed that the cost and delivery dates on the dispersion hardened copper core conductors would not permit their use in this program. Nickel plated (10% Ni), nickel clad (28% Ni) and stainless steel clad (28% type 410) copper wire were chosen as candidates for the 538 C mercury vapor environment. Nickel clad and Inconel clad silver wire were chosen as candidates for the 850 C potassium vapor environment. Lengths of .050" and

.100" dia. OFHC copper wire were obtained for trials for making chrome plated and iron plated copper wire for exposure trials.

4.2.2 Exposure Test Results

Duplicate specimens of nickel plated copper (10% Ni), nickel clad copper (28% Ni) and stainless steel clad copper (28% type 410) were exposed to mercury vapor at 538 C for 340 hours. Weight and appearance changes are listed in Table 2. The nickel plated copper conductors completely disintegrated during the test and portions of the copper core in the nickel clad conductor disappeared probably due to pin holes in the cladding.

Micrographs of the before and after exposure samples of the nickel clad (28%) and stainless clad (28%) copper conductor are shown in Figures 4 through 8. Sample WH3-B was a 340 hour rerun 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 5.)

Samples of the Ni plated, Ni clad and stainless steel clad copper wires were also exposed to potassium vapors at 850 C for 172 hours. On sample WK3 (Figures 8 and 9) penetration of both cladding and core and extensive "gassing" of the core were found. Gassing of the core and voids as a result of the reaction between K and Cu extended about 25% of distance from surface of conductor to center. There was also an extensive diffusion of nickel into the copper which would result in lowering of electrical conductivity of the section. Grain growth in the core was not appreciable, being about .225 mm average grain size both before and after exposure.

Figure 10 is a 100X micrograph of nickel plated (10%) copper wire before exposure to metal vapors. Figure 11 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 WK-3 with gassing being more extensive. The cladding surface was eroded. Resistance of the wire to metal vapor was unsatisfactory. Since the nickel in 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 is not objectionable.

Figures 12 and 13 show the cross section of Oxalloy 28, stainless steel clad copper wire before exposure to any metal vapors. Figure

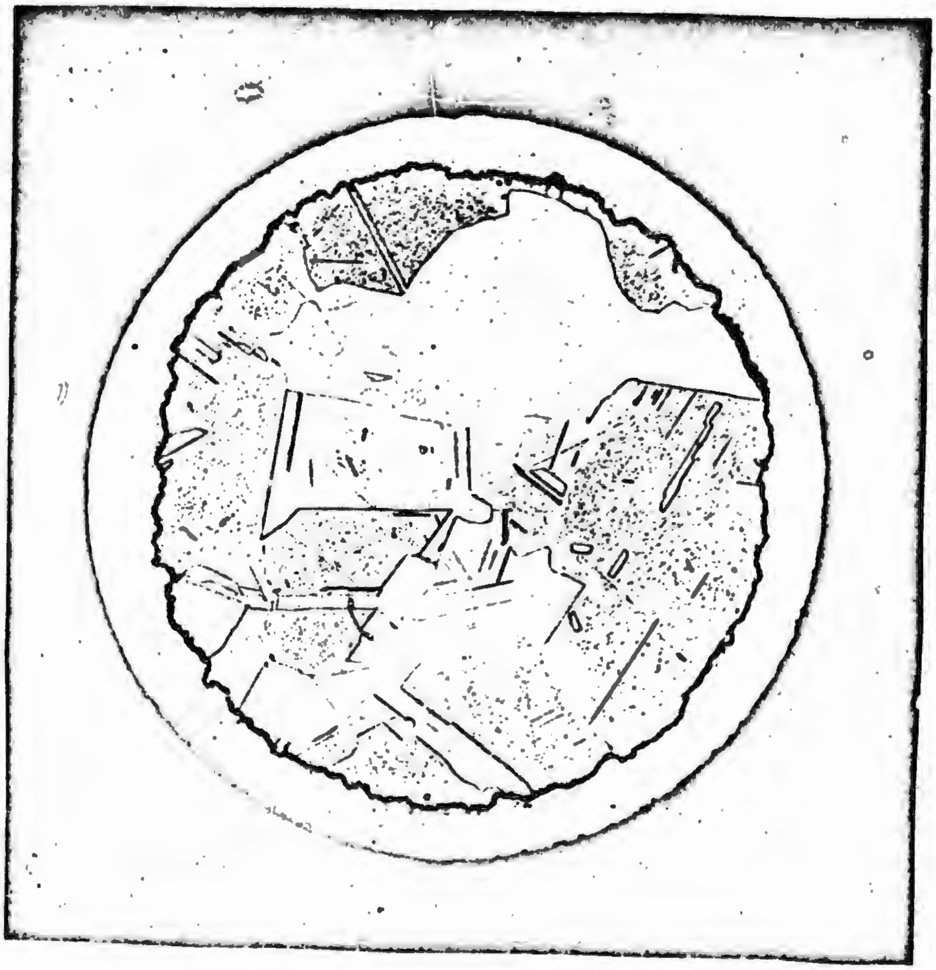


Figure 4. Nickel Clad (28%) Copper Wire Before Metal Vapor 100X Ni-Cu WH-3B C-1293

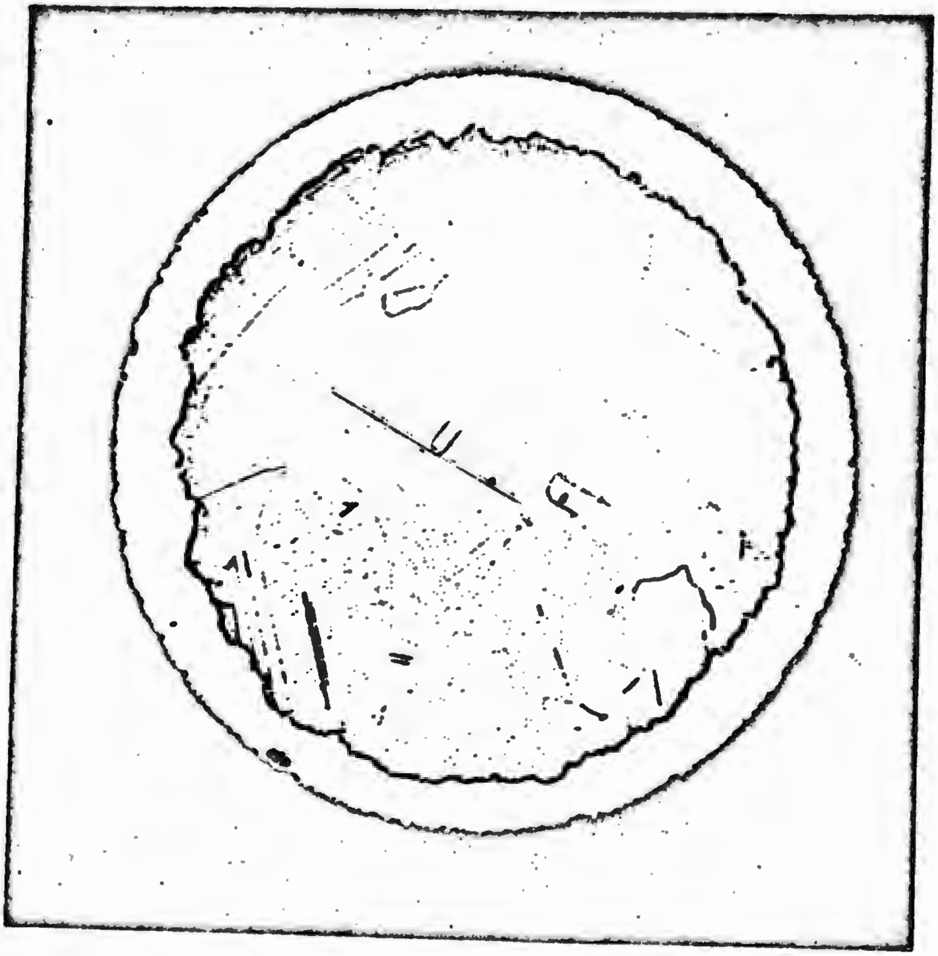


Figure 5. Nickel Clad (28%) Copper Wire After 340 Hours Exposure to Mercury Vapor at 538 C - Second Series of Tests - 100X Ni-Cu WH-3B C-1293

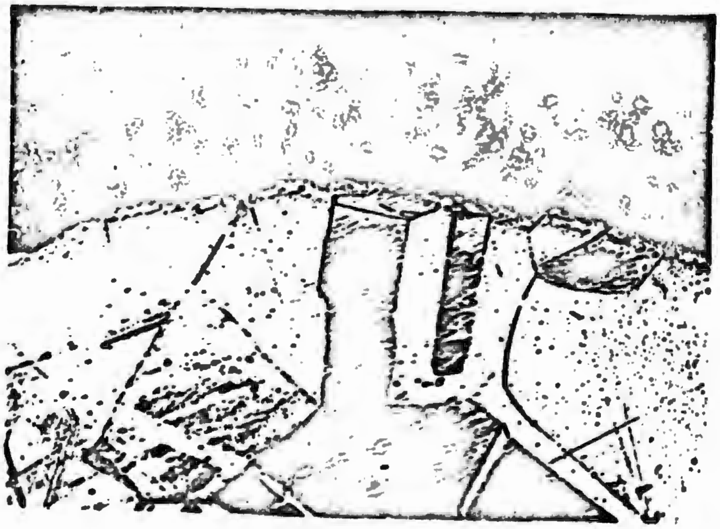


Figure 6. Oxalloy 28, Stainless Steel Clad (28%) Copper Before Metal Vapor Exposure 250X SS Clad CU-S C-0982

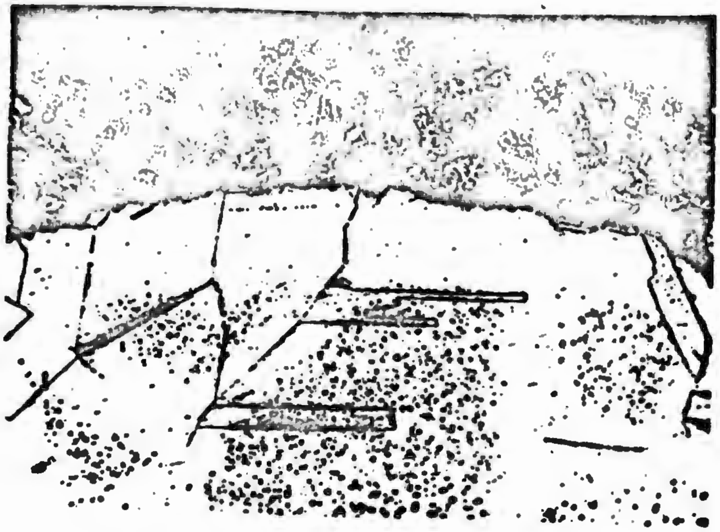


Figure 7. Oxalloy 28, Stainless Steel Clad (28%) Copper After 340 Hours Exposure to Mercury Vapor at 538°C - 250X SS Clad CU-7 C-0982

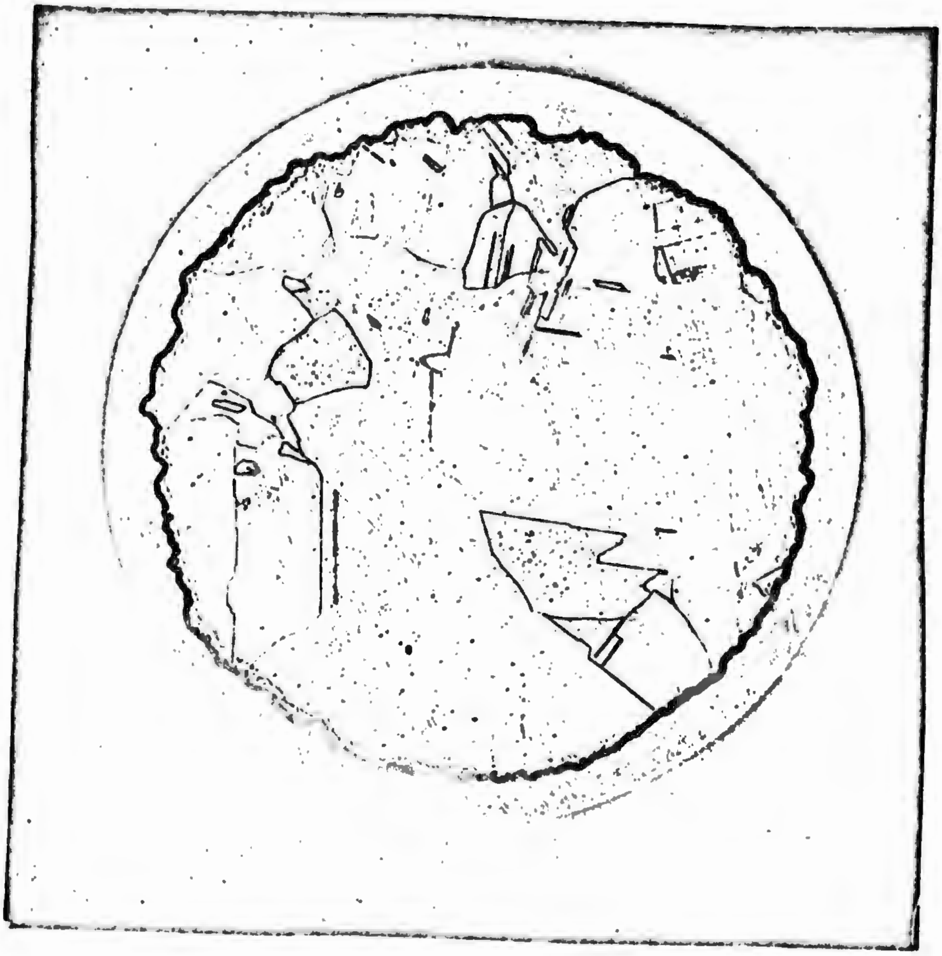


Figure 8. Nickel Clad (28%) Copper Wire Before Metal Vapor Exposure - 100X Ni-Cu WK-3 C-1145

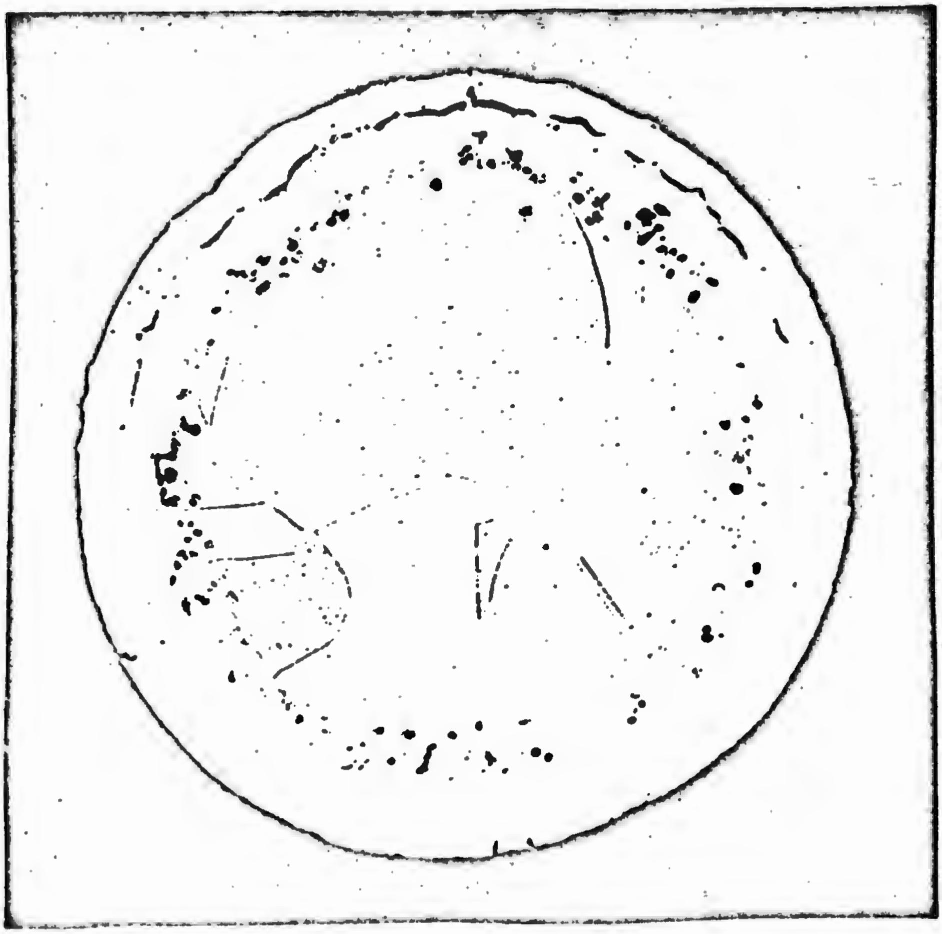


Figure 9. Nickel Clad (28%) Copper Wire After 172 Hours Exposure to Potassium Vapor at 850 C - 100X Ni-Cu WK-3 C-1145

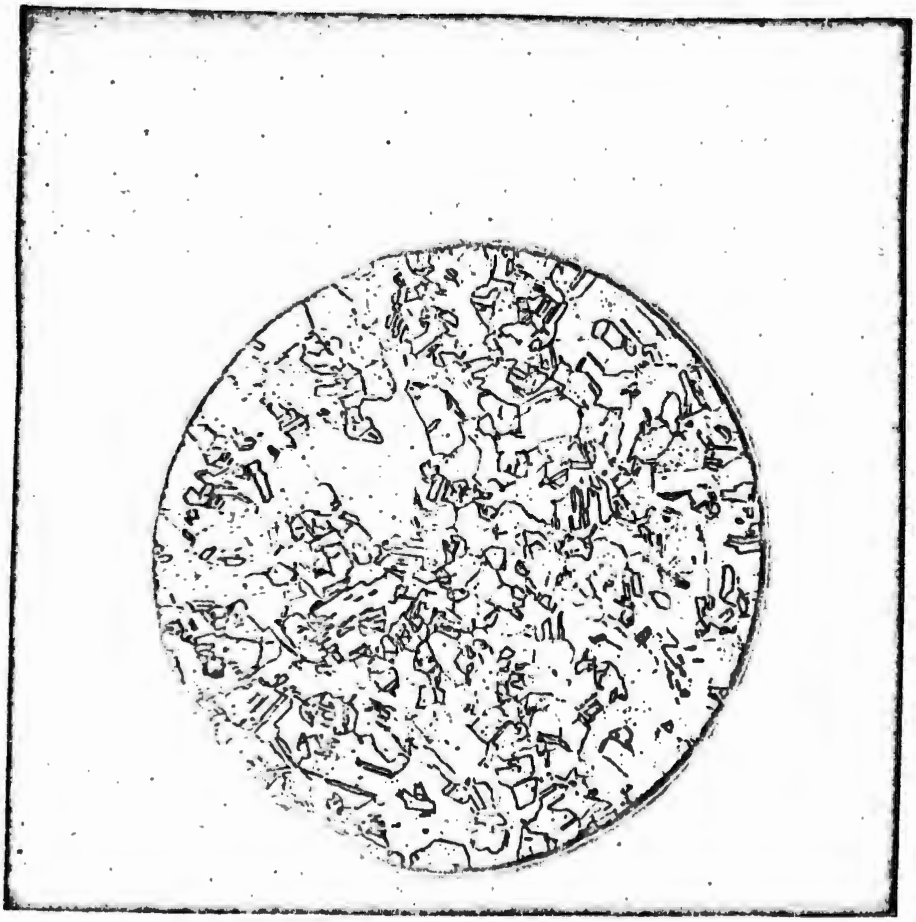


Figure 10. Nickel Plated (10%) Copper Wire Before Metal Vapor Exposure - 100X Ni-Cu WK-1 C-1146

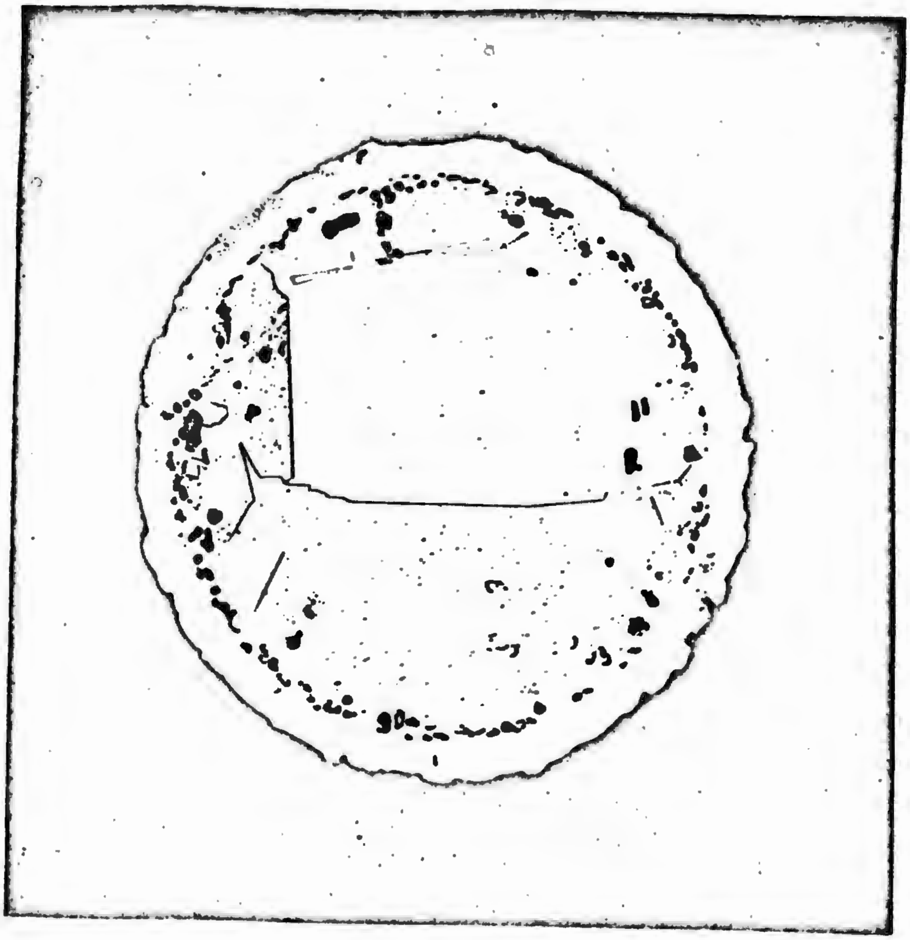


Figure 11. Nickel Plated (10%) Copper Wire After 172 Hours Exposure to Potassium Vapor at 850°C
100X Ni-Cu WK-1 C-1146

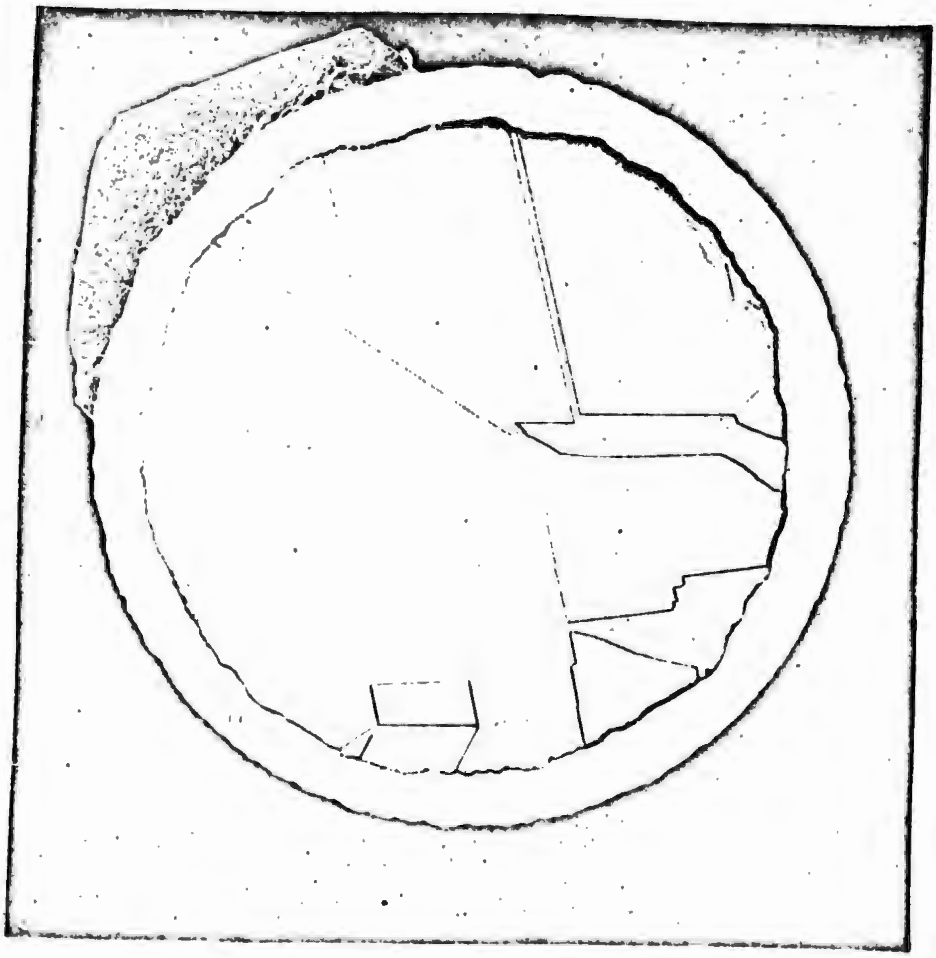


Figure 12. Oxalloy 28, Stainless Steel Clad (28%) Copper Before Metal Vapor Exposure - 100X Oxalloy WK-5 C-1147

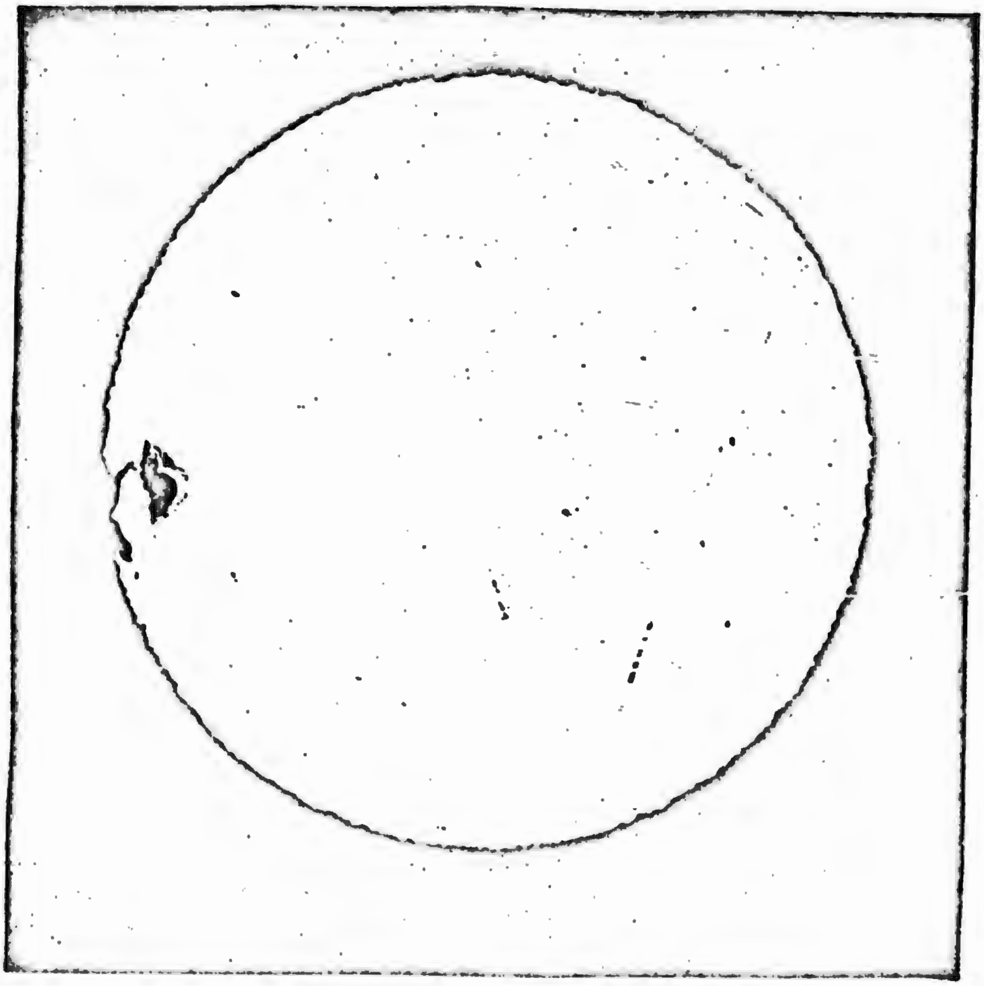


Figure 13. Oxalloy 28, Stainless Steel Clad (28%) Copper After 172 Hours Exposure to Potassium Vapor at 850°C. Sample Unetched - 100X .28 SS Clad Cu Wire Treated Wk-5 C-1147

13 is a 100X, micrograph of an unetched wire showing a fault in the cladding and attack on the copper core after 172 hours exposure to potassium vapor at 850 C. Figure 14 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 7 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 13 is believed due to 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.

A 170 hour exposure of AWG No. 8 Ni clad Ag purchased from Sylvania to potassium vapor at 850 C did not produce any noticeable change in the wire. The ends of the wire had sealed by means of a 7 mil Ni electroplate.

4.2.3 Tensile Strength Measurements

The room temperature tensile properties of Oxalloy 28 were determined.

The ultimate tensile strength was 44,000 psi with a 15% elongation (dia. .051").

The late delivery of the Inconel clad silver wire precluded a thorough metallurgical study of it.

4.3 Electrical Tests

4.3.1 Testing in Argon Environment

4.3.1.1 Test Method and Circuit for Conductors

Conventional 4-terminal technique was used in measuring the electrical conductivity of all conductor samples. Figure 15 depicts the basic circuit. The potential and current connections were made with small stainless steel clamps. The conductivity measurements were made with an ammeter-potentiometer and checked with a Kelvin bridge. Each conductor tested was about 12 inches in length and the potential points were carefully connected 10 inches apart along the wire. The conductors were heated to temperature in a Vycor

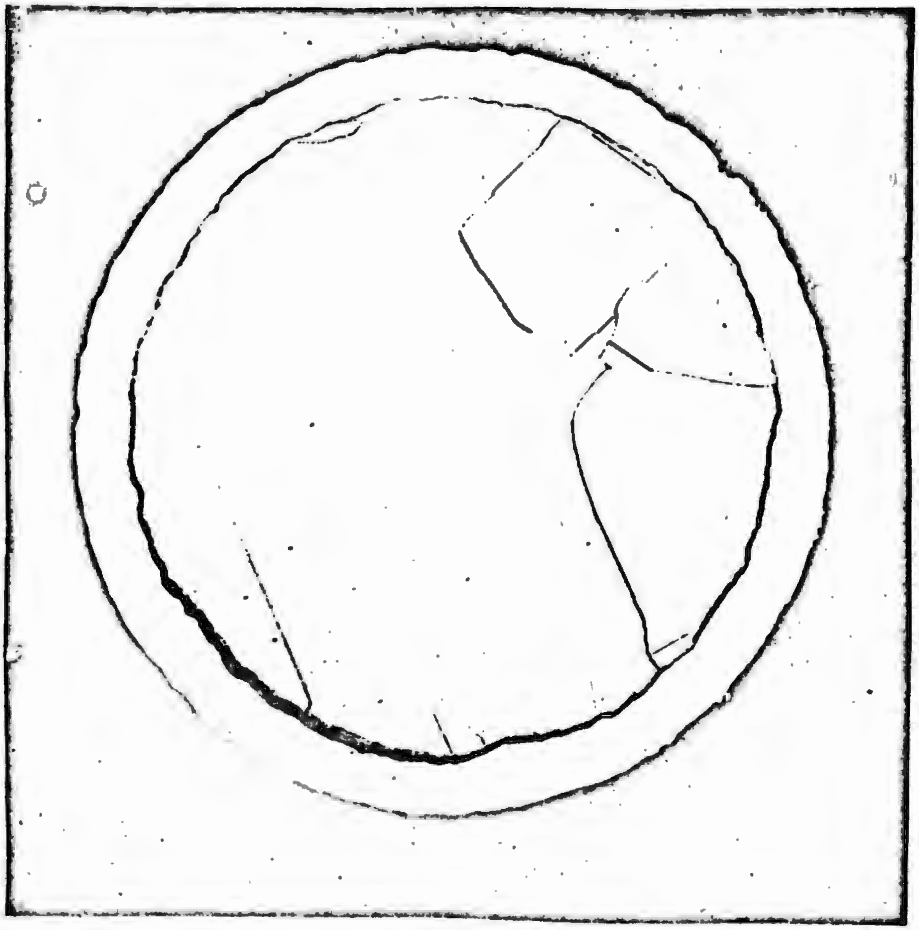
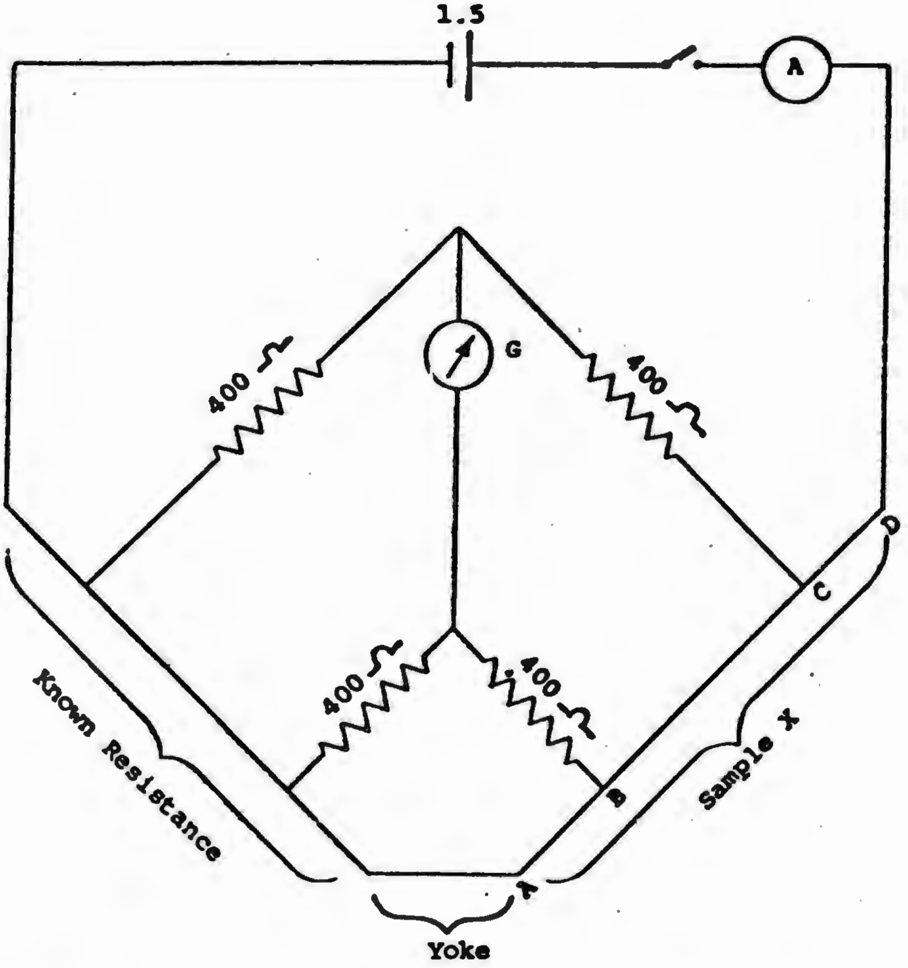


Figure 14. Oxalloy 28, Stainless Steel Clad (28%) Copper After 172 Hours Exposure to Potassium Vapor at 850°C. Sample Etched - 100X Oxalloy WK-5 C-1147



The yoke resistance is close to zero. There are four leads to the sample. Leads at B and C are used in the bridge circuit for potential and virtually no current passes through them. Leads at nodes A and D supply the current to produce the voltage drop between B and C.

Fig. 15 - Bridge Circuit for Resistivity Measurements on Conductors

combustion tube. Figure 16 depicts the electrical measurement set up. Each conductor sample was suspended by four nickel lead-in wires which in turn were supported by alumina ceramic members. A small tube was provided at each sealed-end to permit a continuous flow of commercial high purity argon gas (lcfh) through the combustion tube.

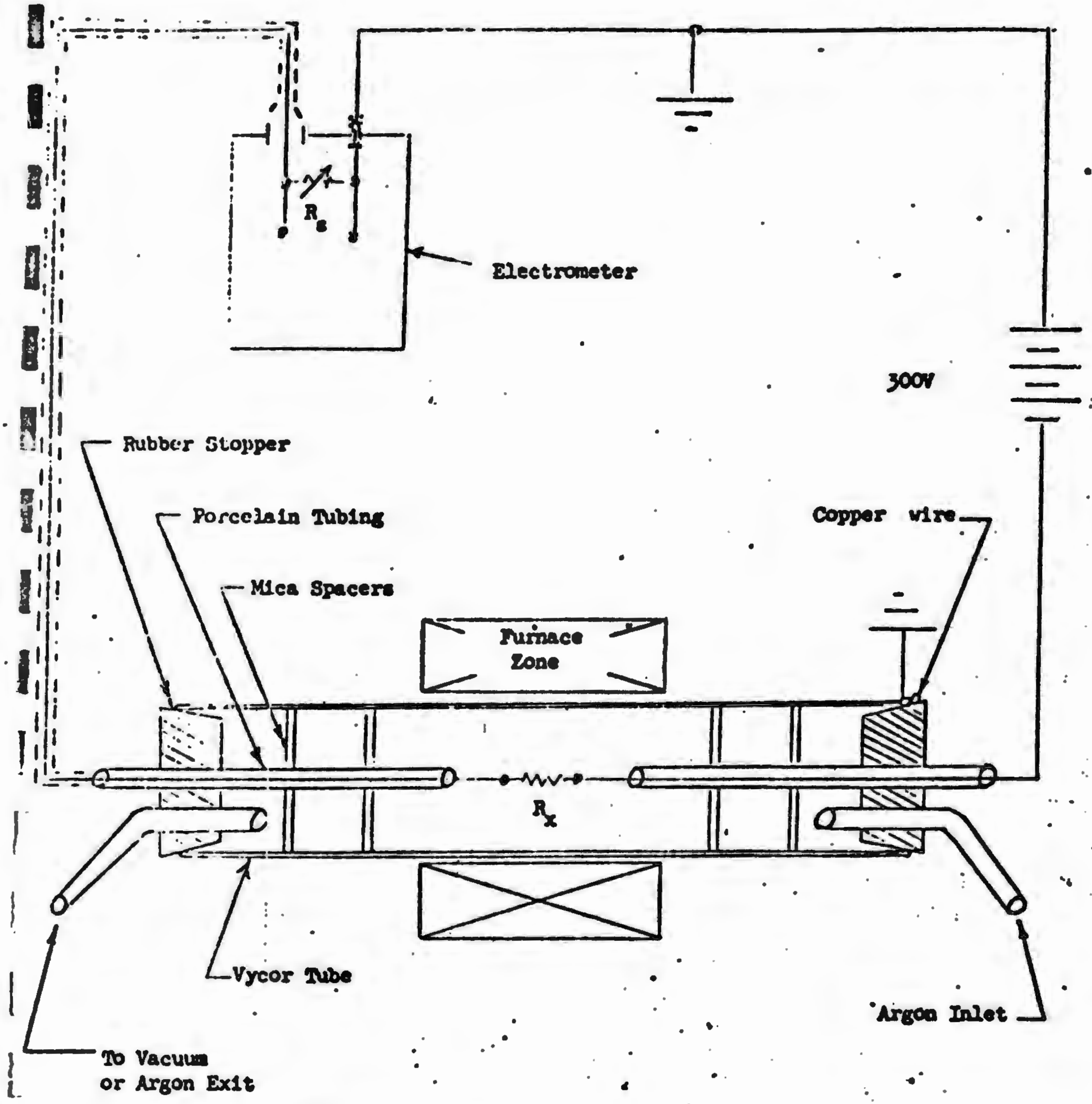
4.3.1.2 Conductors for Hg Vapor Service - Conductivity Vs Temperature

Pre and post thermal aging electrical conductivity-temperature data was secured to 538 C for AWG 16 conductors of commercial grade copper, Oxalloy 28, chrome plated OFHC copper and iron plated OFHC copper. Information on the specific composition of each of these conductors is presented in the section covering "conductivity versus temperature aging". The conductivity-temperature data for bare copper and "Oxalloy 28" conductor samples are shown on Figures 17 and 18. Also plotted on the figures are the conductivity vs temperature data obtained after the samples had been aged at 530 C in argon for 500 hours.

4.3.1.3 Conductors for Hg Vapor Service - Conductivity Vs Temperature Aging

Electrical conductivity measurements were made on samples of commercial grade copper, "Oxalloy 28", chrome plated copper, and iron plated copper as they were thermally aged at 538 C for 500 hours in atmospheres of argon. All samples were AWG 16 gauge and the commercial grade copper samples were included to check on our ability to measure electrical conductivity. "Oxalloy 28" is a copper conductor cladded with 28% stainless steel. The surface plate on each of the chrome and iron plated copper samples was about two mils.

The measured and calculated conductivity values for the commercial grade copper sample are shown in Figure 19. The measured conductivity of Oxalloy 28 is compared with the calculated value for commercial copper in Figure 20. The calculated conductivity 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



(All leads suspended in Air)

Figure 16

Diagram of Insulation Resistance Measuring Apparatus

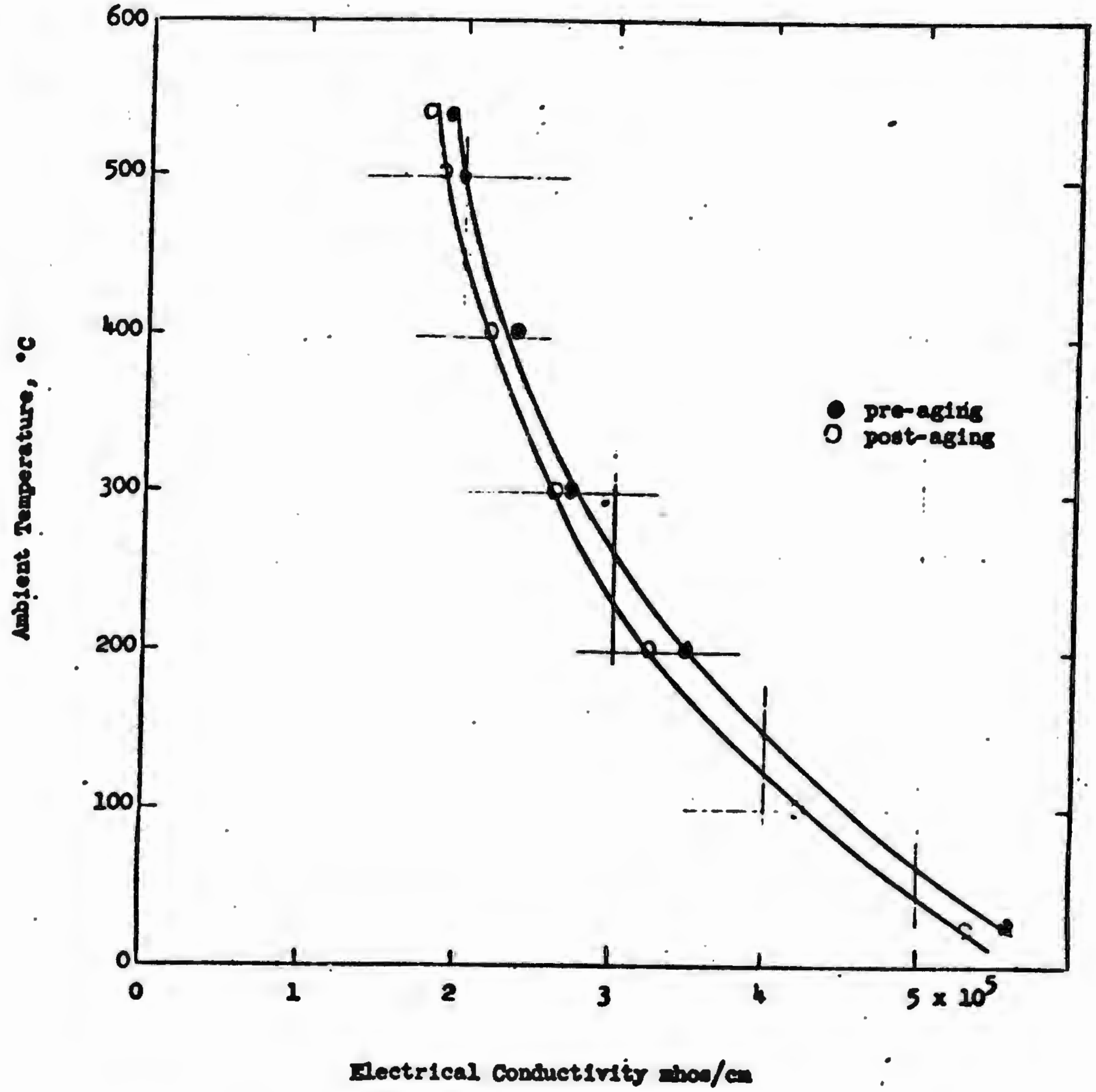


Figure 17- Pre- and Post-Aging Characteristics of Bare Copper Wire at Temperatures to 540°C In Tank Argon.

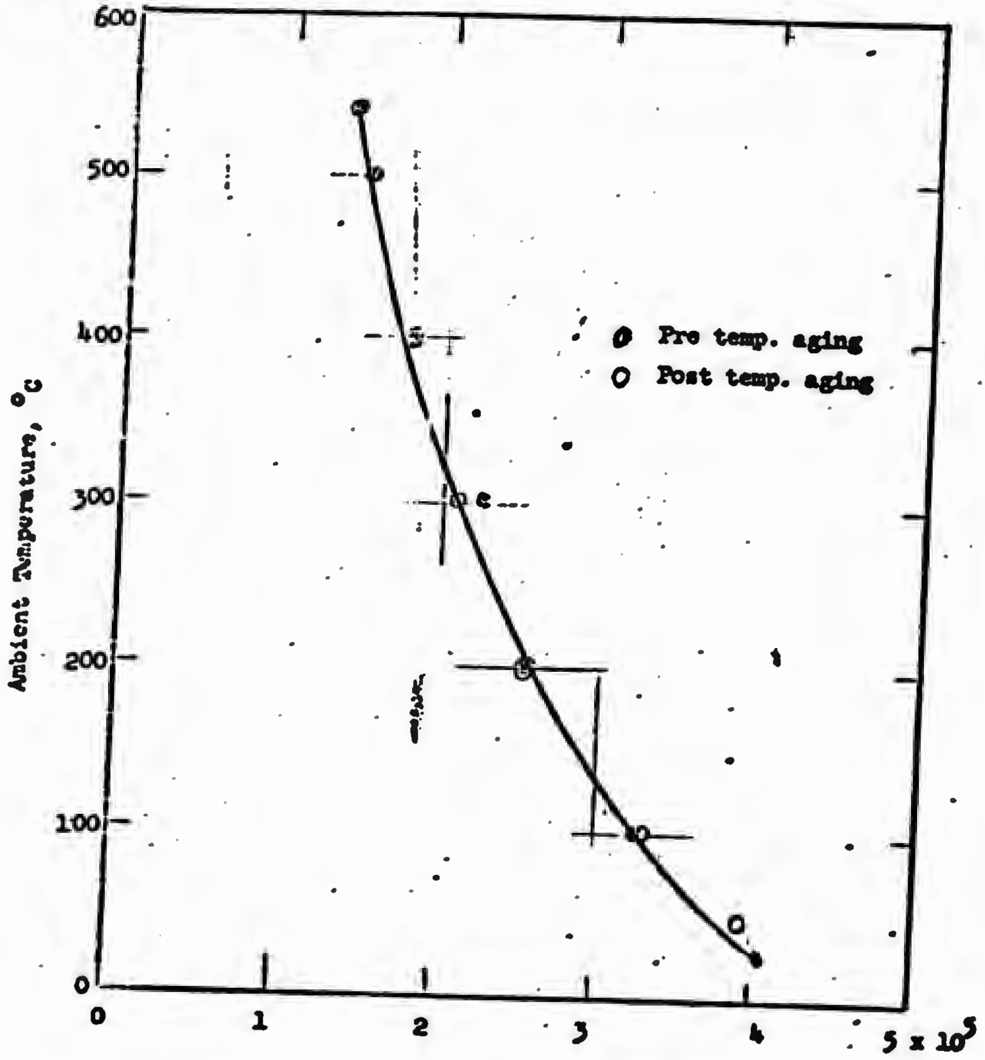


Figure 18 Pre and Post Aging Conductivity - Temperature Characteristics of "Oxalloy 28" in Argon.

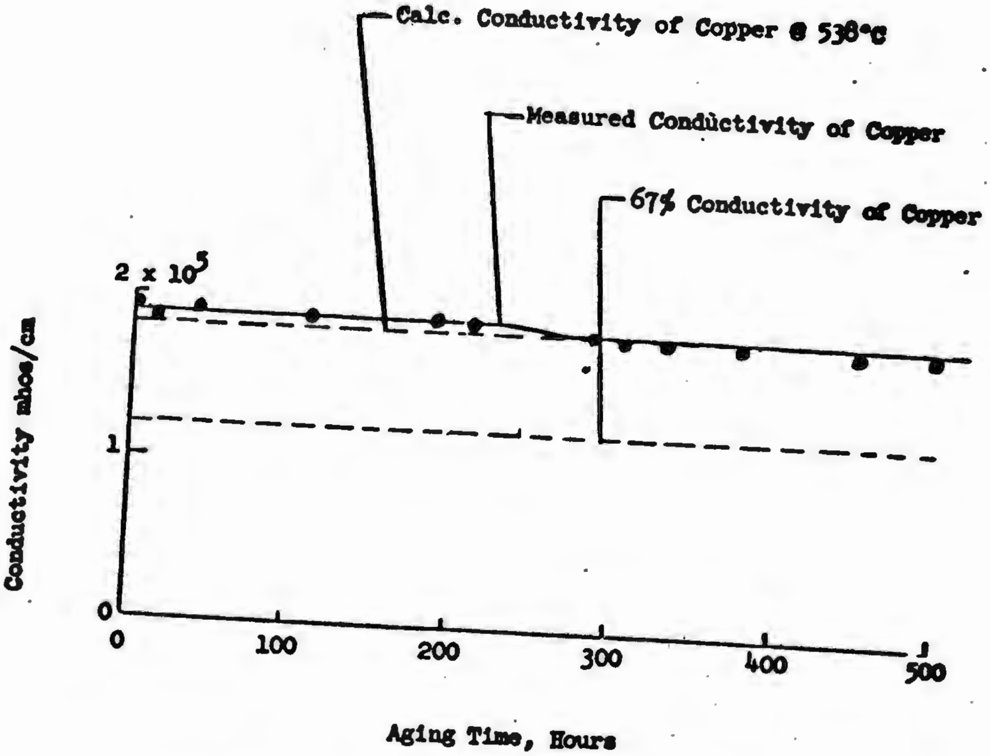


Figure 19- Temperature Aging-Conductivity Characteristics of Copper Wire in Tank Argon at 540°C.

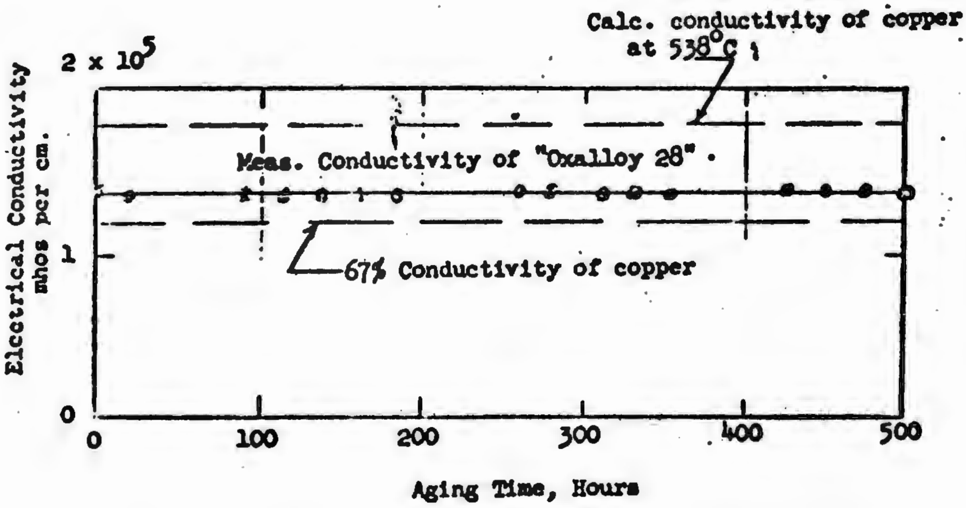


Figure 20. Temperature Aging - Conductivity Characteristic of "Oxalloy 28" in Argon at 538°C.

pure 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%. The pre and post aging conductivity temperature data obtained on the bare copper, Oxalloy 28, iron plated OFHC copper and chrome plated OFHC copper indicated no adverse effects due to thermal aging in 538 C argon for 500 hours. The surfaces of all sample conductors showed degrees of darkening; however, this apparently had little effect on their measured electrical conductivities.

The calculated resistivity for commercial copper is 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 slight 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.

Results of electrical conductivity measurements of all conductors are shown in Table 3. The conductivity value shown for each conductor represents an average of about 15 measurements made during its thermal aging time. The respective electrical conductivities of each conductor remained quite constant throughout their 500 hour thermal aging periods.

It is noted that the measured electrical conductivity of copper at 538 C and the calculated value agree within 2%. The close agreement with actual measurements justifies usage of the calculated electrical conductivity of copper as a standard to compare with measured values of other conductors.

The electrical conductivities of all samples shown in Table 3 are well above the lower allowable limit (67% of copper).

A 5-inch length of "Oxalloy 28" wire (No. 16 gauge) previously exposed to 538 C mercury vapors for 360 hours was additionally aged at the same temperature for 500 hours, in argon. Electrical conductivity data were secured for this conductor as it thermally aged in argon, and is shown in Table 3.

TABLE 3
AVERAGE MEASURED ELECTRICAL CONDUCTIVITY OF VARIOUS CONDUCTOR SAMPLES WHILE THERMAL AGING AT 538 C FOR 500 HOURS IN ARGON

	Samples As Received		Samples Pre-Exposed to Mercury Vapors	
Sample	Conductivity, mhos-cm^{-1}	% Calculated Conductivity of Copper at 538 C	Conductivity, mhos-cm^{-1}	% Calculated Conductivity of Copper at 538 C
Bare Commercial Copper	1.82×10^5	102	----	----
Chrome-Plated Copper	1.73×10^5	97	----	----
Iron-Plated Copper	1.55×10^5	87	----	----
"Oxalloy 28"**	1.37×10^5	77	*1.35×10^5	77

*Pre-exposed to 538 C mercury vapor for 360 hours.

**Stainless Steel clad-copper conductor (28% S/S by vol.).

Average conductivity of the pre-mercury exposed "Oxalloy 28" conductor is nearly identical in value to that found for unexposed "Oxalloy 28". It is concluded that the electrical conductivity of "Oxalloy 28" is unaffected by exposure to mercury vapors at a temperature of 538 C for a period of 360 hours.

4.3.1.4 Conductors for K Vapor Service - Conductivity Vs Temperature Aging

Three 12-inch long wire conductors were thermally aged at 850 C in purified argon. One conductor is 20% nickel clad silver wire and is 128 mils in diameter (No. 8 AWG). The second conductor is "Oxalloy 28", 28% stainless steel clad copper, and is 51 mils in diameter (No. 16 AWG). Two samples of "Oxalloy 28" were tested. A No. 16 gauge commercial grade copper wire was also thermally aged to provide a means for checking our ability to measure electrical conductivity at 850 C.

The measured and calculated conductivity values for the commercial grade copper sample are shown in Figure 21. The measured electrical conductivity of copper at 850 C and the calculated value agree within 3%. This close agreement with actual measurements justifies usage of the calculated electrical conductivity of copper as a standard to compare with measured values of other conductors. The measured conductivity of "Oxalloy 28" is compared with limiting values of conductivity as determined from conductivity calculations for copper in Figure 22. It is noted that the conductivity of "Oxalloy 28" decreased with time and fell below the lower allowable limit, 67% of the electrical conductivity of copper, after 100 hours of aging at 850 C.

Results of electrical conductivity measurements of conductors are shown in Table 4. None of these conductors had previous aging in potassium vapor. The conductivity value shown for each conductor represents an average of about 15 measurements during its thermal aging time.

The conductivity of "Oxalloy 28" decreased with time and fell below the lower allowable limit, 67% of the electrical conductivity of copper, after 400 hours of aging at 850 C. As previously reported, a second test of a similar sample of

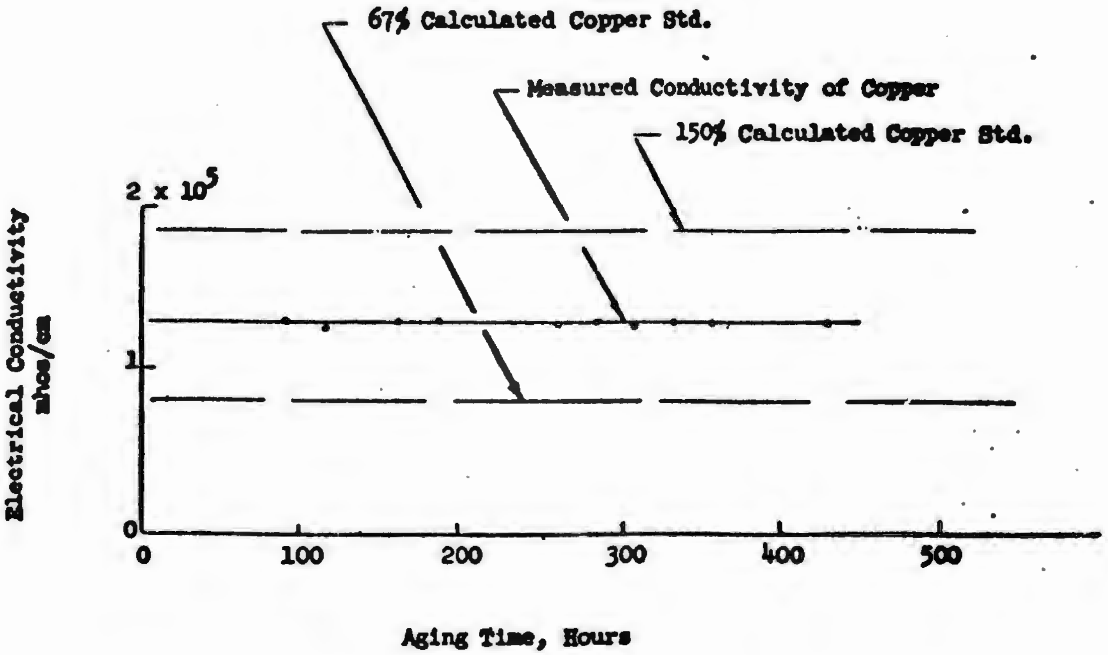


Figure 21- Temperature Aging-Conductivity Characteristics of Copper Wire in Purified Argon at 850°C.

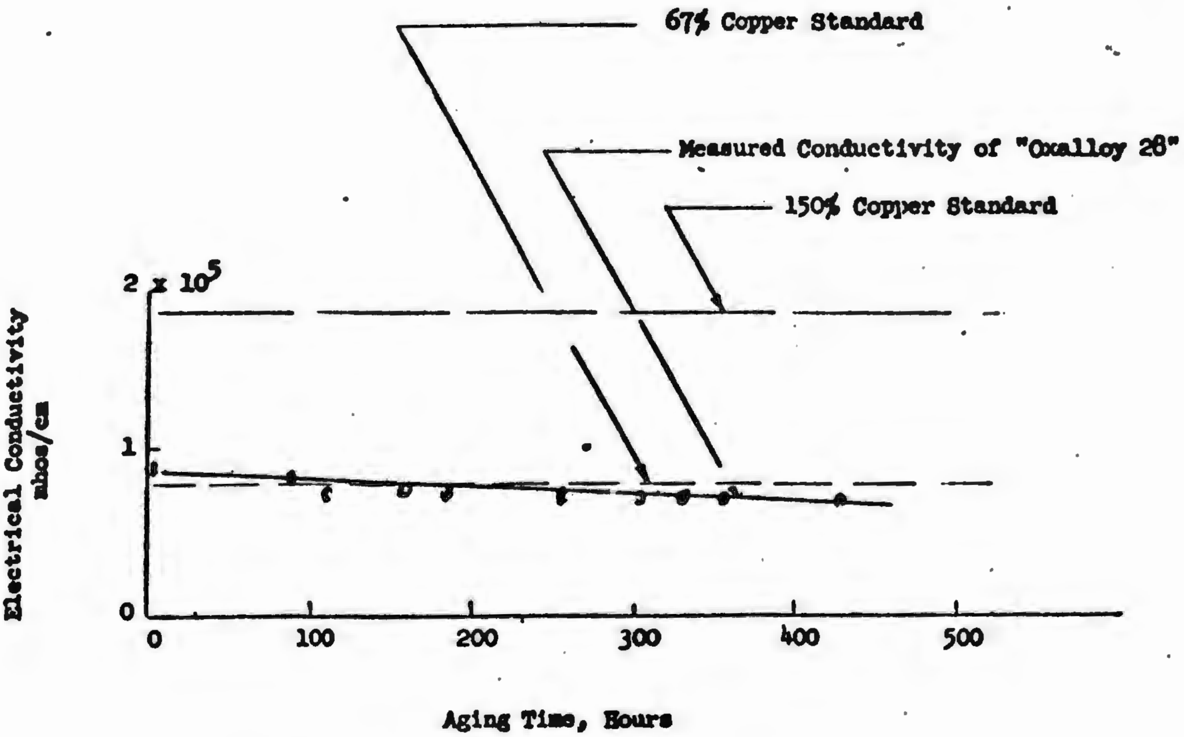


Figure 22- Temperature Aging-Conductivity Characteristics of "Oxalloy 28" in Purified Argon at 850°C.

TABLE 4
AVERAGE MEASURED CONDUCTIVITY OF VARIOUS CONDUCTOR SAMPLES WHILE THERMAL AGING AT 850 C FOR 500 HOURS IN ARGON

	Samples as Reveived	
Sample	Conductivity mhos-cm^{-1}	% Calculated Conductivity of Copper at 850 C
Bare Commercial Copper**	1.35×10^5	103
Nickel Clad - Silver*	1.1×10^5	89
"Oxalloy 28"	Failed after 500 hours***	

*20% Nickel Clad - Silver

**28% Stainless Steel Clad - Copper

***Test of a second specimen failed after 100 hours.

"Oxalloy 28" failed after 100 hours of thermal aging. Electrical conductivity of the nickel clad-silver wire at 850 C remained constant throughout the 500-hour aging period. The average measured conductivity of this conductor, 1.1 x 10^5 mhos per centimeter, is 89% of the calculated value for pure copper at 850 C. Thermal aging had very little effect on this conductor as the pre and post conductivity-temperature data agree quite well.

4.3.1.5 Test Method and Circuit for Insulators

Figure 16 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 at 850 C was three orders of magnitude greater than the resistance of subsequent specimens measured and, consequently, no significant error in measurement came from that source.

The leakage resistance measurements of each insulation material was made while the sample was suspended within the vycor combustion tube. Evaporated gold electrodes were applied to each sample leaving a 1/4-inch space between. Electrical connections were made to the evaporated gold surfaces with gold foil held in contact by small stainless steel parallel jaw clamps. Prior to making resistance measurements, a vacuum (100 microns) was drawn on each 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.

4.3.1.6 Insulators for Hg Vapor Service - Resistance Vs Temperature

The electrical volume resistivities of seven materials were determined in an atmosphere of tank argon at 538 C ambient temperature. Resistance values were measured with 300 volts d-c between the electrodes.

The materials and their respective electrical resistivities are shown in Table 5. Four of the material samples had been previously exposed to 538 C mercury vapors for 260 hours prior to the electrical measurements in argon. However, only one material, beryllia, allows direct comparison of the effect exposure to 538 C saturated mercury vapor has on its electrical resistivity. Pre-exposing beryllia to mercury vapors resulted in a drastic reduction in its volume resistivity from 10^{10} to 10^4 ohm-inches at 538 C. Of the four materials previously exposed to saturated mercury vapors, strontium zirconate (Y-628) has the highest measured electrical volume resistivity, 1.4×10^7 ohm-inches. This value is comparable to the "as received" hot pressed magnesia sample (1.9×10^7 ohm-inches).

4.3.1.7 Insulators for K Vapor Service - Resistance Vs Temperature

Figure 23 shows the plot of resistance measurements made on a 1/2-inch diameter 1/16-inch thick sapphire disk in an atmosphere of argon to a temperature of 850 C. 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}. The electrical volume resistivities of five additional materials were determined in an atmosphere of tank argon at 850 C ambient emperature. These materials and their respective electrical resistivities are shown in Table 6. Three of the samples had been previously exposed to 850 C potassium vapor for 165 hours prior to the electrical measurements in argon. However, only one material, hot pressed magnesia, allows direct comparison of the effect exposure to 850 C saturated potassium vapor has on its electrical resistivity. Pre-exposing hot pressed magnesia to potassium vapors resulted in a reduction of its volume resistivity from 2.5×10^6 to 7.8×10^3 ohm-inches at 850 C. Of the three materials previously exposed to saturated potassium vapors strontium zirconate (Y-628) has the highest measured electrical volume resistivity, 6.5×10^4 ohm-inches. Strontium zirconate (Y-628) showed the highest resistivity of those materials measured which had been pre-exposed to mercury vapors at 538 C.

TABLE 5
ELECTRICAL VOLUME RESISTIVITY OF VARIOUS MATERIALS AT 538 C IN ARGON

	Material	Volume Resistivity, Ohm-Inches As Received	 Pre-exposed*
(CX-14)	Beryllia	1.7×10^{10}	----
(CH-14)	Beryllia	----	1.1×10^{4}
(CX-12)	Sapphire	6.5×10^{9}	----
(CX-17B)	Sintered Boron Nitride	6.0×10^{8}	----
(CX-10)	Hot Pressed Magnesia	1.9×10^{7}	----
(CH-7B)	Alumina (Coran)	----	3.5×10^{5}
(CH-18)	Strontium Zirconate (Y-628)	----	1.4×10^{7}
(CH-19)	Strontium Zirconate (Y-760)	----	4.2×10^{4}

*Pre-exposed to 538 C mercury vapor for 260 hours.

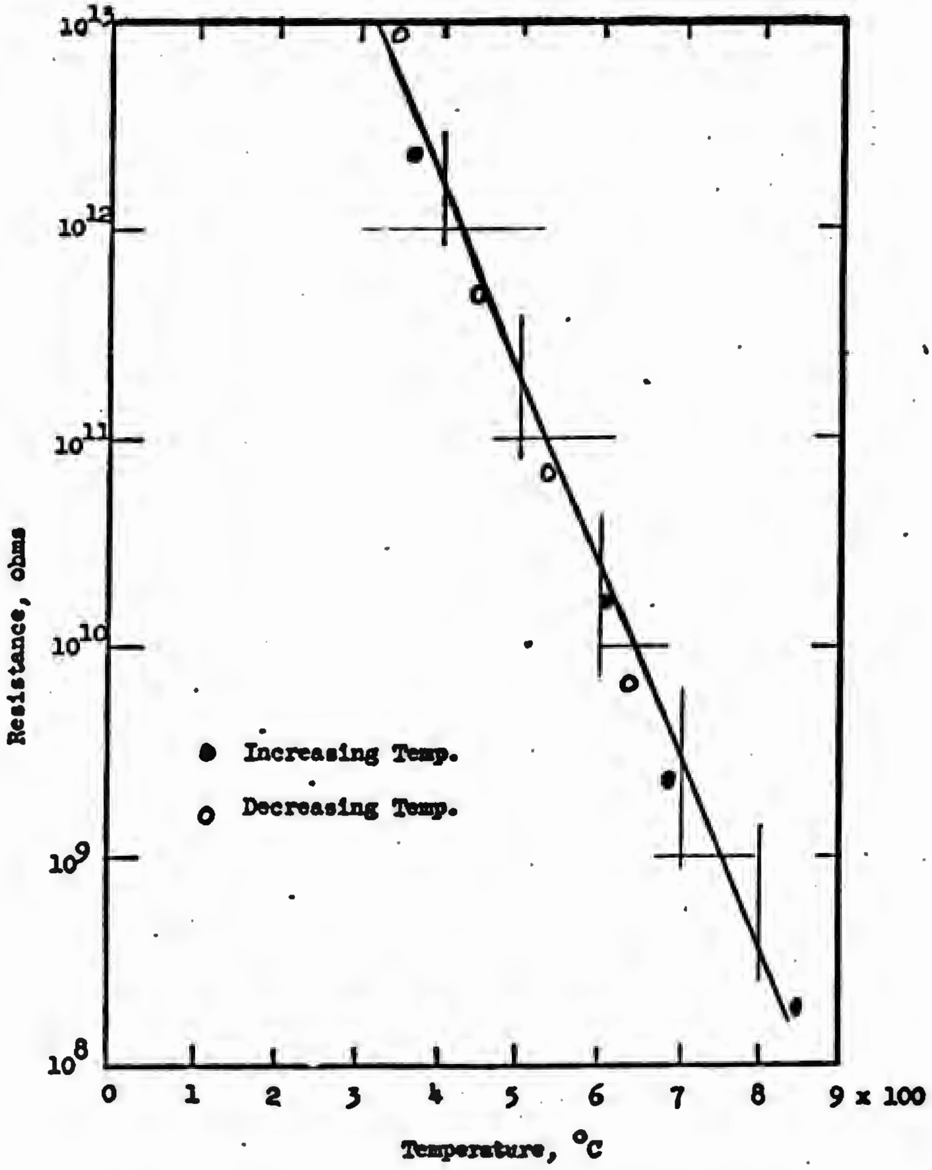


Figure 23 - Resistance - Temperature Characteristics of Sapphire in Argon.
(1/2" dia. disk - 1/16" thick)

TABLE 6
ELECTRICAL VOLUME RESISTIVITY OF VARIOUS MATERIALS AT 850 C IN ARGON

	Material	Volume Resistivity, Ohm-Inches As Received	 Pre-exposed*
(CX-12)	Sapphire	1.5×10^7	----
(CX-14)	Beryllia	6.0×10^6	----
(CX-10)	Hot Pressed Magnesia	2.5×10^6	----
(CK-10)	Hot Pressed Magnesia	----	7.8×10^3
(CX-17B)	Sintered Boron Nitride	6.0×10^5	----
(CK-19)	Strontium Zirconate (Y-760)	----	1.4×10^4
(CK-18)	Strontium Zirconate (Y-628)	----	6.5×10^4

*Pre-exposed to 850 C potassium vapor for 165 hours.

The electrical leakage resistance of a second sapphire disk sample was made while it was heated to a temperature of 850 C in an argon atmosphere. Tantalum electrodes were sealed to the 1/2-inch diameter sapphire disk with a 95% zirconium-5% beryllium brazing composite. One of the two electrodes was located at the disk's periphery and the second at its center. The peripheral electrode consisted of a 1/2-inch diameter tantalum tube which was 2-1/2-inches in length. The central electrode was a 1/32-inch diameter tantalum pin and it extended through the 1/2-inch thick disk. The measuring voltage applied to these electrodes was 260 volts d-c. The leakage resistance at 850 C measured 5.7×10^7 ohms. This value compares favorably with that previously found for the thinner (1/16-inch) but equal diameter (1/2-inch) sapphire disk and measured with a different electrode configuration, 1.5×10^8 ohms.

4.3.2 Measurements in Mercury Vapor

4.3.2.1 Test Capsule

The capsule for this work is similar to the corrosion test capsule except that the crimped-welded end is replaced by the lead-in insulator using a suitable seal. To permit charging the electrical test capsule without having the lead-in insulator in contact with the liquid metal, two modifications have been made. The Swagelok fitting cap was modified to provide a 5-10cc reservoir. Molten K can be placed in the reservoir and allowed to cool and solidify. The capsule can be assembled and closed by the normal procedure. For the Hg, which is liquid at room temperature, the modified Swagelok would be used; however, a socket extension on the electric wrench will permit tightening the capsule in an inverted position (Swagelok at the bottom).

Initial tests to determine the electrical characteristics of the lead-in insulator in argon and mercury vapor must be made prior to mounting the insulated conductor specimens in the capsule because the lead-in would be a parallel circuit. A five mil diameter nickel wire wrapped tightly around a 3/4-inch long section of the insulated wire would serve as one electrode and the conductor itself as the other electrode in the volume resistivity and electric breakdown tests. The nickel wire would be spot welded to the capsule wall and the insulated conductor would be spot welded to the lead wire through the lead-in insulator.

Five test capsules were prepared in which commercial lead-in insulators were used. Three capsules incorporated Ceramaseal (Series 801 and 805) 85% alumina to Kovar seals (using 72% Hg-28% Cu). The units had alumina insulators that were in the shape of a cylindrical tube about 1/2" long 1/2" outside diameter, and 1/4" wide inside diameter. A Kovar flange cap with a threaded stud was silver-copper brazed to the top and a Kovar flanged cylinder to the bottom exterior portion of the alumina tube. The lower flange was heliarc welded or furnace brazed to 4-inch long stainless steel tubes which formed a reservoir for the liquid mercury. After charging the capsule with mercury, the steel tube was sealed with a steel "Swagelok" fitting. The test procedure used is the same as described in the corrosion test section. Two other capsules incorporated U. S. Stoneware Alite C-500 cable end seals heliarc welded to 1/2" diameter nickel tubes.

4.3.2.2 Pre Mercury Vapor Exposure Tests

The electrical leakage resistance of an Alite C-500 cable-end capsule seal was determined while heating to a temperature of 538 C in an atmosphere of argon. The electrical characteristic obtained from this measurement was intended to be compared with similar data on modified and, or, mercury charged C-500 type sealed capsules. The measuring voltage was 285 volts d-c. Electrical leakage of the insulation seal at 538 C was found to be 5.1×10^6 ohms.

4.3.2.3 Testing in Mercury Vapor

The measuring circuit described in Section 4.2.1.5 for tests conducted on insulation in an argon environment was used for measuring surface and volume resistance of insulators in the metal vapor environment.

A number of Ceramaseal (Series 801 and 805) alumina to Kovar seals were successfully welded to a 1/2" diameter stainless steel (304) tube. These assemblies were charged with mercury, sealed, and submitted for electrical resistivity measurement over a 540 C temperature range.

Attempts were made to measure the electrical leakage resistance of the five alumina-Kovar seals at a temperature of 538 C while one side of each seal was exposed to saturated mercury vapor. Figure 24 shows the test assembly. In every case mercury leaks developed, either in the Kovar flange or the alumina-Kovar seal, prior to attainment of the desired temperature conditions for electrical measurement.

Mercury leakage occurred in one capsule, using a Ceramaseal insulator, at 300 C. The resistivity of the insulator at this temperature was 5 x 10^8 ohm per square. Figure 25 plots the data obtained in this insulator in argon and mercury vapor.

A second type of alumina to Kovar seal (Alite cable end seal) was sealed to a 1/2" diameter nickel tube. The capsule was then loaded with mercury and sealed. Although exposure to high temperature mercury vapor did not cause leakage at the ceramic to metal joint, the assembly ruptured at an apparently weak Kovar to Kovar joint inherent in the design of the seal. This joint was strengthened with a high melting brazing alloy (Incusil-Ag/Cu eutectic + 15% In) after which the test was repeated. This modified mercury charged capsule developed a leak when its temperature was raised to near 500 C. Inspection revealed that although the reinforced flange sustained mercury attack, the brazed metal-ceramic joint did not. Two other capsules incorporating Alite C-500 cable end seals started to leak about 400 C. Resistance values of 4 x 10^7 ohms were measured prior to signs of leakage with an insulated temperature of 400 C and a mercury reservoir temperature of 380 C.

4.3.3 Measurements in Potassium Vapor Environment

4.3.3.1 Pre Potassium Vapor Exposure Tests

The electrical leakage resistance of an alumina (Lucalox) disk incorporated as part of a tantalum-alumina-molybdenum seal was determined in an atmosphere of tank argon at 850 C. This metal-to-ceramic seal employs a 95% zirconium-5% beryllium brazing composite. A 1/32" diameter molybdenum pin extended through and was sealed at the center of this disk. A 1/2" tantalum tube was sealed to the periphery of the 1/16" thick alumina disk. These metal-ceramic seals were found vacuum tight, prior to and after cycling to 850 C, with a helium-type leak detector. The measured electrical leakage resistance of this seal at 850 C in argon was 9.7 x 10^7 ohms.

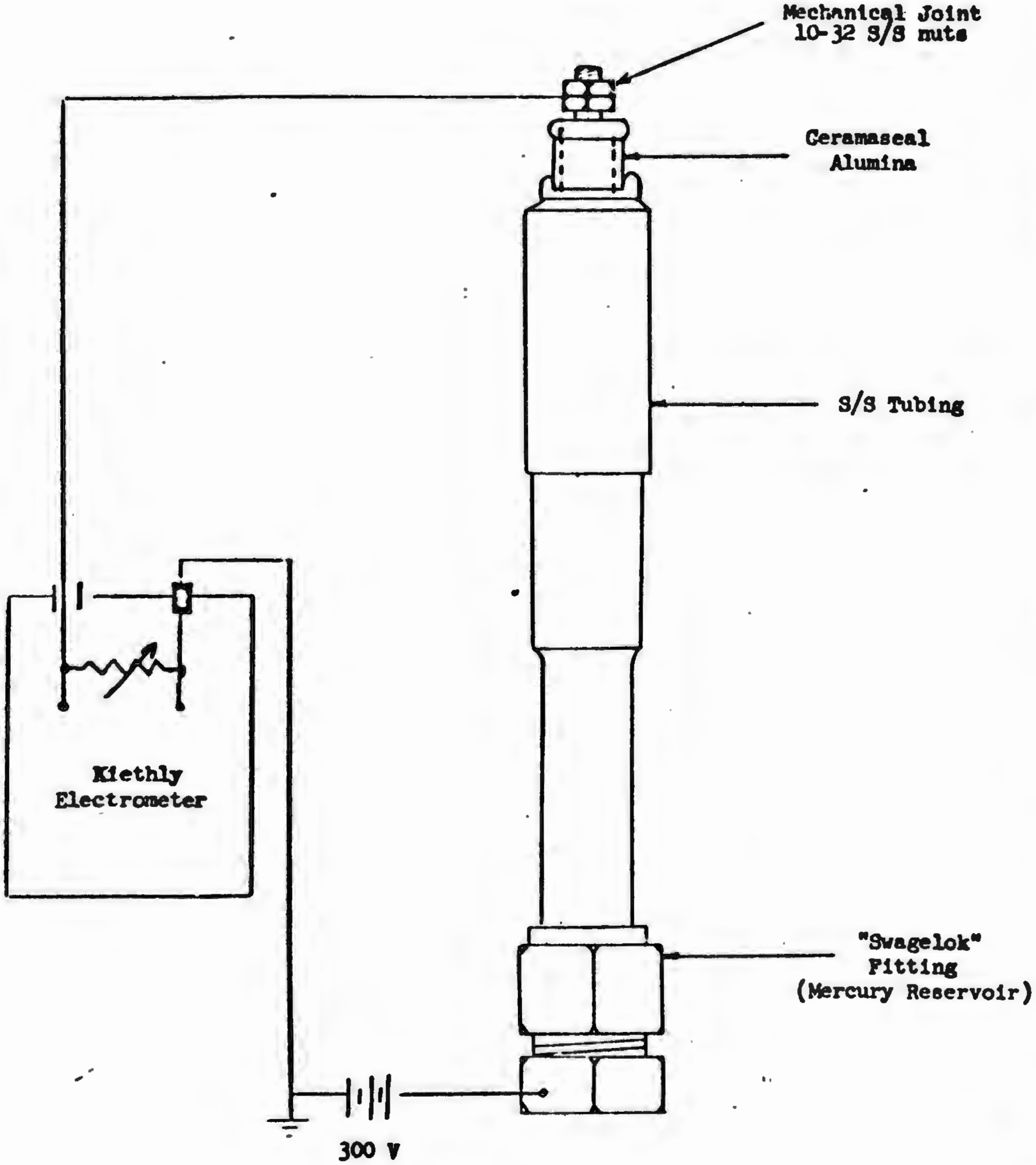


Fig. 24 - Capsule and Circuit Used to Measure Electrical Resistance of Ceramaseal Lead-In In Hg Vapor Environment.

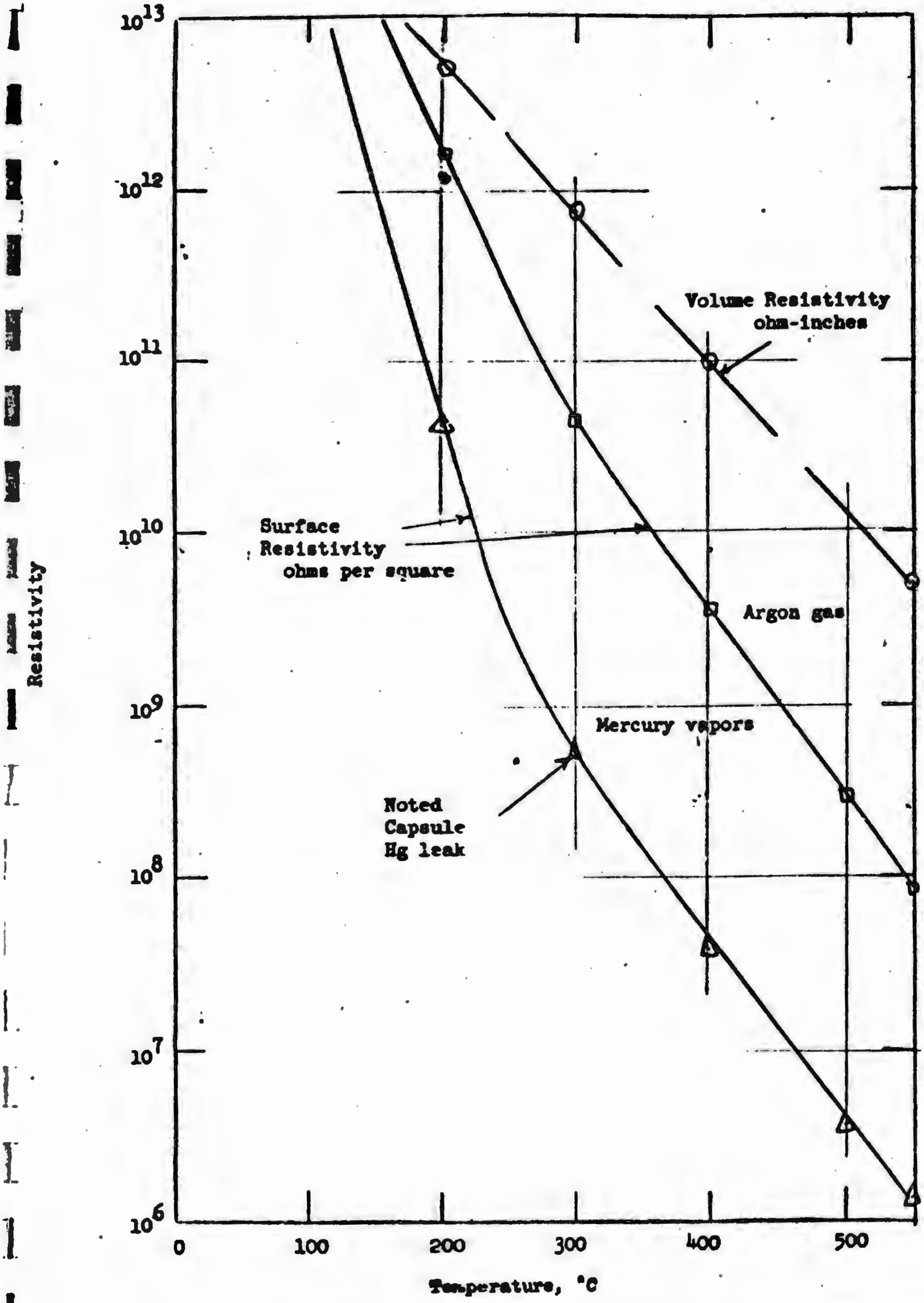


Figure 25 - Temperature - resistivity characteristic of "Ceramaseal" alumina.

The data is plotted in Figure 26.

Leakage resistance of a similarly designed capsule with a 1/2-inch thick sapphire disk measured 5.7 x 10^7 ohms at 850 C. (See Section 4.3.1.7).

Electrical leakage resistance measurements were made on a cylindrical tube capsule of alumina (Lucalox) sealed at each end with disks of niobium. The alumina tube is 3-1/2-inches long between metal disks, 5/8-inch outside diameter, and 1/2-inch inside diameter. A leakage resistance of 2.2 x 10^7 ohms was measured at a temperature of 850 C in high purity argon. The data obtained is plotted in Figure 27.

The electrical leakage resistance and volume resistivity of a commercially available insulation-conductor system from Advanced Technology Laboratory was determined at a temperature of 850 C in tank argon. The 1/8" diameter copper conductor of this system was electrically insulated by a 1/32" wall of magnesia powder which was packed in a concentric 1/4" diameter sheath of 304 stainless steel. The measured leakage resistance and volume resistivity of the magnesia in this system are 9.3 x 10^6 ohms per inch and 1.4 x 10^8 ohms-inches, respectively. The electrical volume resistivity of magnesia as applied in packed powder form in this system is about 50 times higher than that previously reported for hot pressed magnesia at 850 C.

A number of conductors previously coated by plasma spraying or vapor deposition of insulation materials were subjected to electrical leakage resistance measurements in an atmosphere of argon. Resistance measurements were made between the conductor core and an outer sheath electrode. The sheath electrode, usually 3/4-inch in length, was made by winding 5-mil diameter nickel wire in a close helix around the conductor insulation. Low leakage resistances were measured across plasma sprayed ceramic coatings of either zirconia or alumina. Three coats averaged 12 mils in thickness. The low resistance values are attributed to surface irregularities in the flame sprayed ceramic coatings. The small diameter wire of the sheath electrode did not bridge all of the shallow areas of the ceramic film and thus low resistance measurements resulted. The data obtained on the zirconia coated Ni rod is plotted on Figure 28.

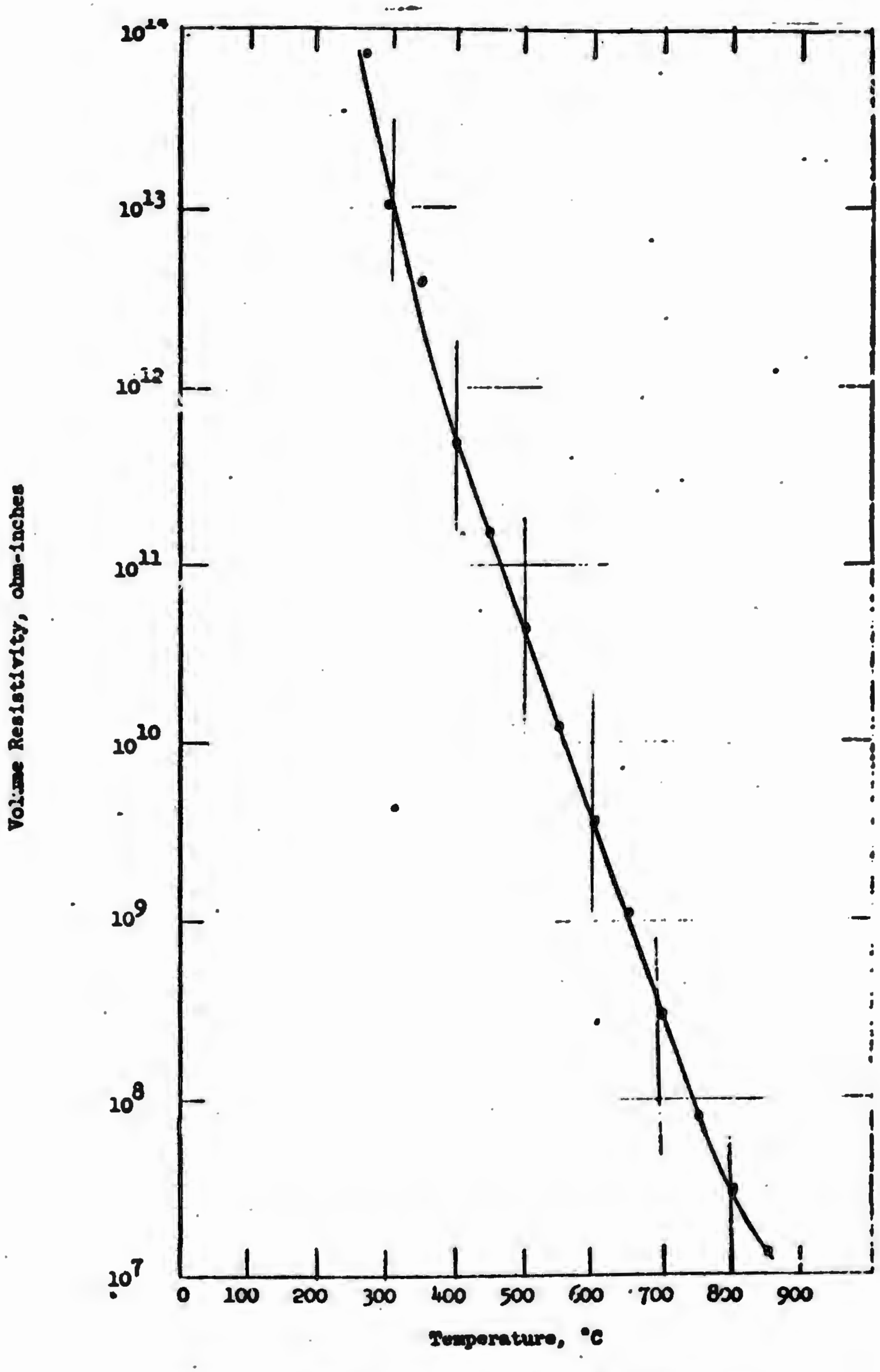


Figure 26 - Resistivity - temp. data of molybdenum - alumina - tantalum seal in argon.

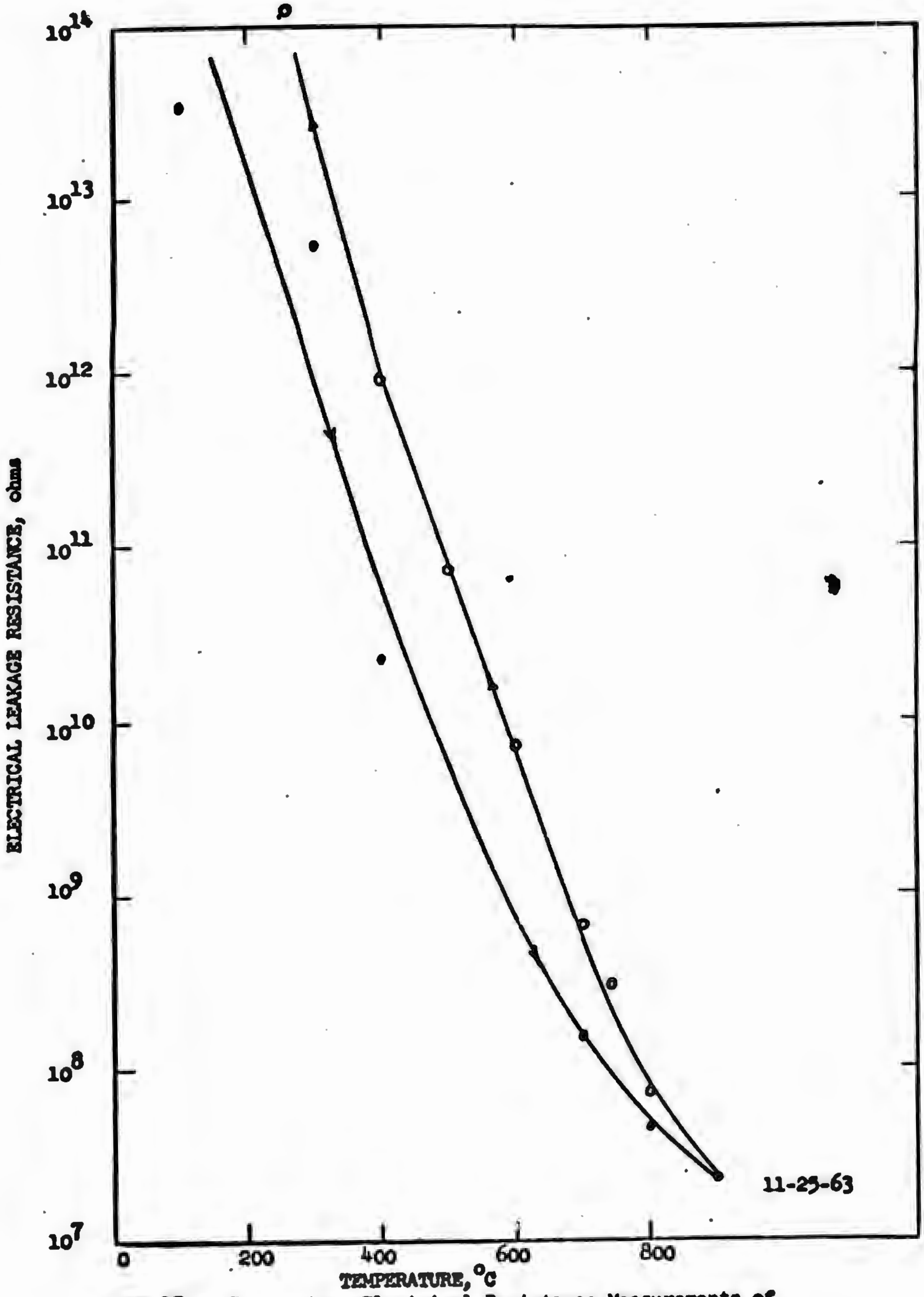


FIG.27 -- Temperature-Electrical Resistance Measurements of an Alumina-Niobium Seal in Argon.

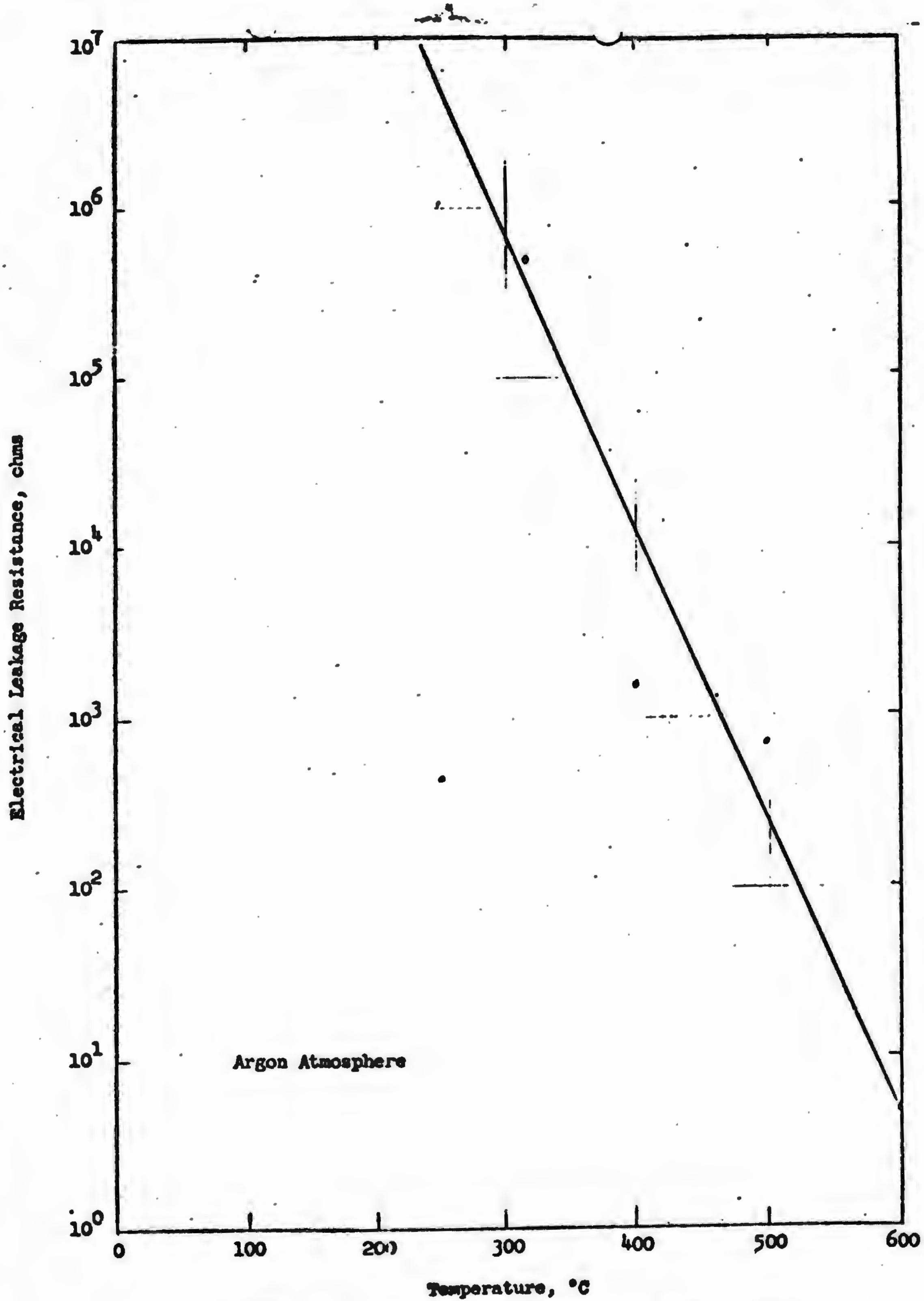


Fig. 28 - Electrical Leakage Resistance of Flame Sprayed Zirconia on a 1/8" dia. Nickel Rod. (12 mil total build)

A rather dense, but thin, coherent coat of aluminum nitride vapor deposited on to a 1/8-inch diameter molybdenum rod was measured electrically. The leakage resistance between the rod and a 3/4-inch long sheath electrode was measured as the sample was heated in argon to 850 C. The resistance decreased from 3.2×10^9 ohm at 100 C to 4.0×10^5 ohm at 850 C.

A nickel-clad silver conductor coated with a 1-2 mil coat of nickel-aluminide, 1-2 mil over-coat of zirconia, and a very thin evaporative final coat of aluminum-nitride was heated to 850 C in argon. The leakage resistance of this compound coating, to a 1/2-inch long sheath electrode, varied from 6.4×10^{13} ohms at 100 C to 1.8×10^4 ohms at 850 C.

4.3.3.2 Testing in Potassium Vapor

The capsule design for the electrical tests was 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 a metallic penetration through it to provide for electrical connection. The sapphire-tantalum tube capsule, described in the last paragraph of Section 4.3.1.7, was charged with potassium. Due to the position of the capsule during charging, the surface of the sapphire disk was covered with liquid potassium and apparently remained "wetted" by the potassium when the capsule was inverted. The leakage resistance at room temperature 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 flow-off 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 heat up. 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 so as to see 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 Ta tube/type 316SS 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 leakage resistance increased from 6 ohms to 9.1 x 10^4 ohms. During this time, the temperature of the capsule near the sapphire disk was about 5C 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 disk 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 a Triplett electronic multimeter (model 850), was infinite at room temperature.

It is concluded that potassium vapor adversely affects the electrical leakage resistance of sapphire. The leakage resistance of sapphire is decreased at least 625 times at a temperature of 850 C in the presence of low concentrations of potassium vapors.

4.3.4 Electrical Breakdown in Metal Vapors

4.3.4.1 Electrical Breakdown

The electrical breakdown voltage of mercury and potassium vapor have been reported and found to obey Paschen's law similar to other gases. The breakdown voltage of mercury vapor was given by Llewellyn-Jones (3) and for potassium vapor by Bratescu (4). These values are given as a function of product of pressure and gap and are plotted in Figure 29 and shown in the table below. The pressure of the metal vapor was obtained from data compiled by the Southwest Research Institute (5).

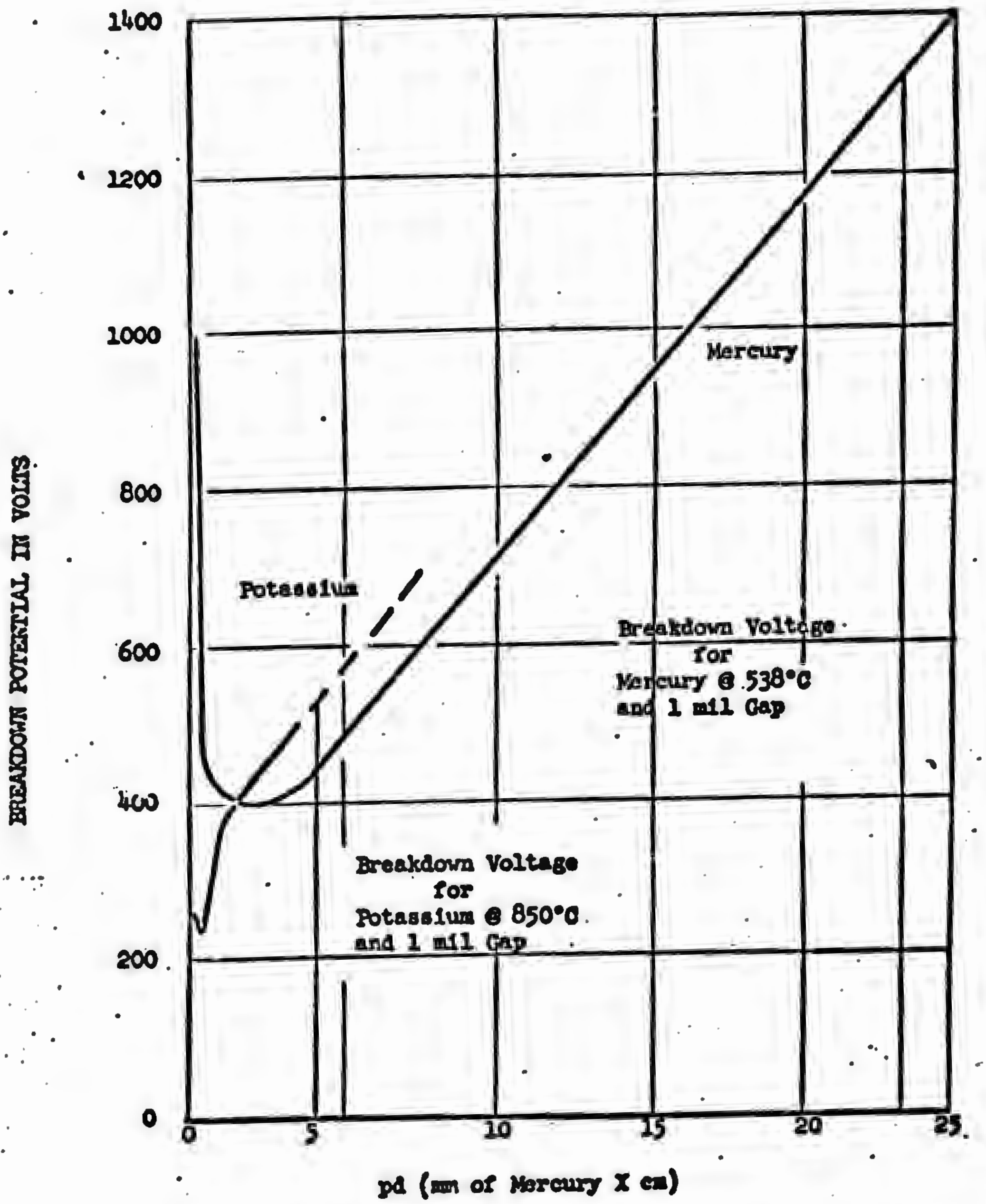


Fig. 29 Paschen Curves for Mercury and Potassium Vapor

Properties of Metal Vapors

Metal	Temp.	Vapor Pressure in mm of Hg	pd* for 1 mil gap	Breakdown Voltage
Hg	538 C	9205	23.4	1330 volts
K	850 C	1655	4.2	540 volts

*p in mm of Hg and d in cm of gap

The voltage breakdown values appear to be high enough to prevent breakdown (flashover) during electrical resistivity testing. Electric strength measurements should be possible if the samples are sufficiently thin so breakdown voltages are below flashover voltage for the pd product.

The data for calculating the electrical conductivity of both mercury and potassium vapor has been obtained from various investigators. This conductivity is important in measuring the insulation resistance of insulators in the metal vapors.

Work done by J. F. Nolan and A. V. Phelps (6) 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 30 and 31 show the drop in resistance as a function of terminal temperature and time.

There was some concern that the saturated K and Hg vapor would also condense out on the lead-in insulator. Initial tests in Hg vapor were attempted where the insulator resistivity

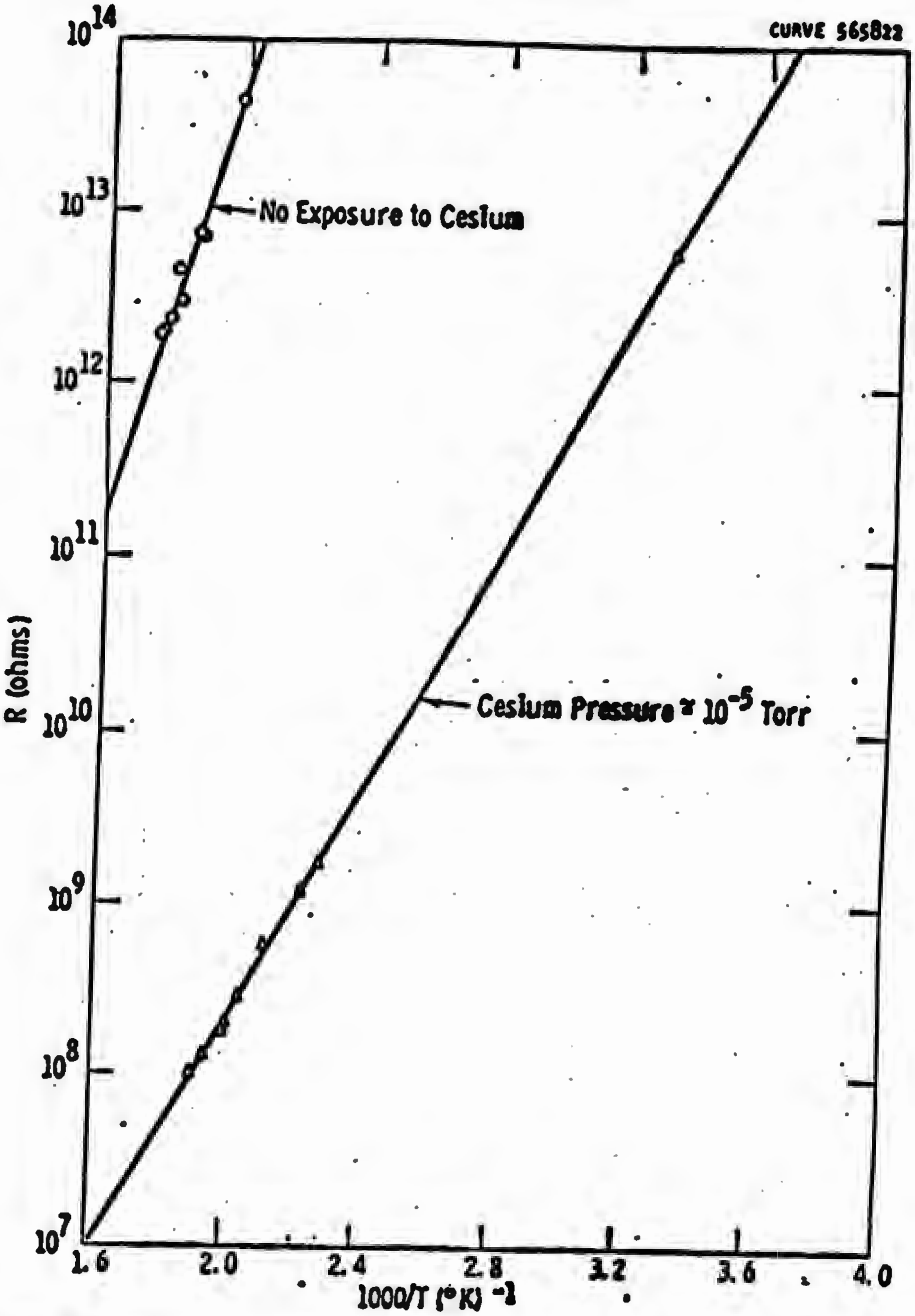


Fig. 30 Leakage Resistance of MgO Terminal vs. $\frac{1}{T}$ where T is the Temperature of the Terminal in °K. The Upper Curve is for No Cesium Exposure; The Lower Curve for a Cesium Vapor Pressure of About 10^{-5} Torr.

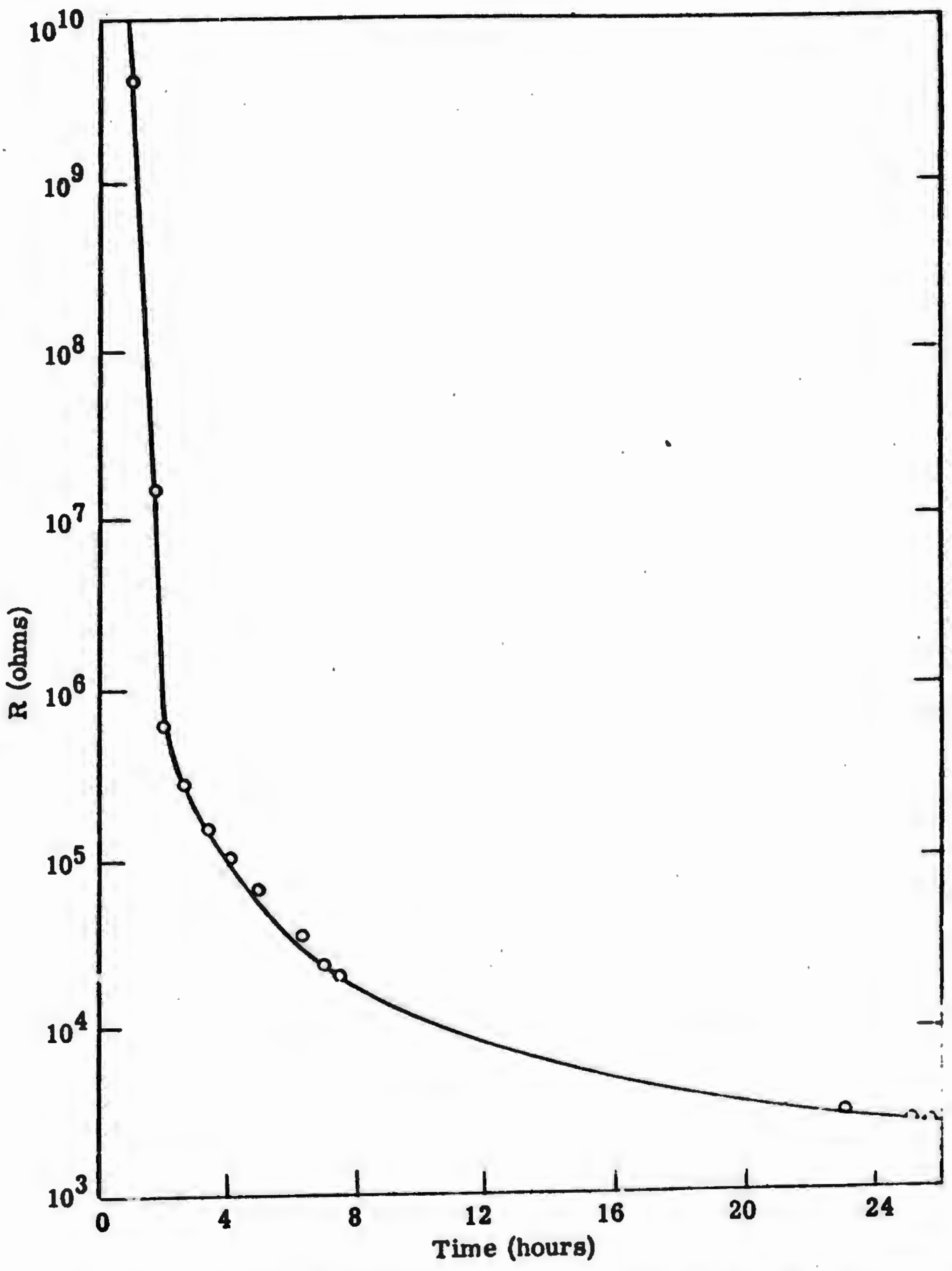


Figure 31. Leakage Resistance of MgO Terminal as a Function of Time After Cesium Reservoir is Raised to Give a Vapor Pressure of 1 Torr. The value of R at Time = 0 is 2×10^{12} ohms

was to be determined as a function of vapor pressure. A special capsule was constructed that would allow the temperature of the Hg reservoir to be slowly raised, while holding the insulator at 540 C. Unfortunately, the test runs were always prematurely terminated by leakage at the ceramic-to-metal seal or capsule tube to cable end unit seal. On Figure 25, a pronounced change in slope is evident in the lower curve at the temperature at which mercury vapor leakage was first noted. A continuation of the initial slope would have shown the surface resistivity of alumina, in near saturated mercury vapor, to be 10 ohms per square at 550 C.

4.4 Ceramic to Metal Seals

4.4.1 Wetting Tests with Brazing Alloys

Wetting tests were initially made in argon, vacuum and hydrogen atmospheres. Small pieces of brazing alloy (100 Mg) were placed on small pieces of high purity alumina (Lucalox). The specimens were placed inside a ceramic tube which, in turn, was placed inside a molybdenum susceptor for induction heating to the desired temperature. In the runs in vacuum the unit was pumped down to 10^{-5} torr prior to heating the samples. Tables 7 and 8 list the results of most of the early wetting tests and Figures 32, 33 and 34 show several of the micro structures of the resultant joints.

A group of "T joints" were made between Lucalox and tantalum specimens with the alloys which appeared most promising in the wetting tests. These specimens were placed in stainless steel capsules with potassium and held at 850 C for 170 hours, and the relative corrosive damage was noted.

A list of the active metal brazing alloy compositions tested and results of the wetting and potassium exposure tests are given in Tables 7 and 8.

Results showed that most of the titanium and zirconium alloys would wet pure alumina. In some of the specimens cracks are formed in the alloy itself or in the alumina upon cooling from the brazing temperature (see Figure 35). The nickel base alloys did not wet the alumina in vacuum, in argon, or in hydrogen. All the brazing alloys exhibit poor resistance to potassium at 850 C, except the following where some adhesion between the brazing alloy and ceramic was noted after exposure:

TABLE 7
BRAZING ALLOYS - POTASSIUM VAPOR CORROSION TESTS

Brazing Alloy	Approx. Joining Temperature	Quality Of Wetting On Alumina	Resistance to (K) (850 C)	Remarks
48% Zr 48% Ti, 4% Be	1060 C	good	Brazing alloy separated from the Lucalox.	Alloy not being considered for making seals at this time.
75% Zr 19% Cb, 6% Be	1050 C	good	Brazing alloy separated from Lucalox.	Alloy rejected because of poor resistance to potassium.
62% titanium 26% iron 8% molybdenum	1200 C	good, but brazing alloy contained cracks.	Brazing alloy separated from Lucalox.	Alloy rejected because of cracking and poor resistance to potassium.
63% titanium 27% iron 10% vanadium	1210 C	good wetting but alloy cracking	Not determined as test capsule leaked.	Not considered as cracking thought to be a deterient.
68% titanium 28% vanadium 4% beryllium	1250 C	adequate	Fair, brazing alloy could be separated with difficulty after exposure.	A seal joint between Lucalox and tantalum was made but severe cracking of Lucalox was encountered.

TABLE 7 (Cont.)
RESULTS OF WETTING TESTS ON LUCALOX (Al_2O_3)

Alloy and Specimen Type	Atmosphere	Temp.	Time at Temp.	Results
Nicrobraz 130, (Ni-base; 3.5-B, 4.5-S, 0.15-C) on Lucalox	Vacuum	1125 C	1-1/2 min.	No wetting.
L.M. Powder (Ni-base; 6.5-Cr, 3.0-B, 4.5-Si, 2.5-Fe, 0.15-C) on Lucalox	Vacuum	1050 C	2-1/2 min.	No wetting.
L.C. Nicrobraz, (Ni-base; 13.5-CR, 4.5-Fe, 3.5-B, 0.15-C, 4.5-Si) on Lucalox	H_2	1200 C		No wetting.
Nicrobraz 60 (Ni-base; 17.0-Mn, 8.0-Si, 0.15-C) on Lucaloz	Vacuum	1335 C	2-1/2 min.	No wetting.
L.M. (Ni-base; 6.5-Cr, 3.0-B, 4.5-Si, 2.5-Fe, 0.15-C) on Lucalox	H_2	1100 C	3 min.	No wetting.
L.M. with Titanium Hydride	Vacuum	1050 C	2 min.	Appeared to wet ceramic but brazing alloy could be peeled off.
95% Zirconium, 5% beryllium on Lucalox	Vacuum	1300 C	2 min.	Lucalox wetted.

TABLE 7 (Cont.)
RESULTS OF WETTING TESTS ON LUCALOX (Al_2O_3)

Alloy and Specimen Type	Atmosphere	Temp.	Time at Temp.	Results
95% Zr-5% Be Brazed Type 304 Stainless to Lucalox	Vacuum	1300 C	2 min.	Lucalox wetted first then stainless joined to wetted area. Good joint.
95% Zr-5% Be Kovar to Sapphire	Vacuum	1100 C 1300 C	1 min. 1 min.	Sapphire was first wetted with alloy, then joined to Kovar. Good joint (see photo).
95% Zr-5% Be Assembly Lucalox disc to tantalum tube, molybdenum wire through center of Lucalox.				Parts assembled without pre-wetting. Both joint made at once, joints were lead tight.

TABLE 8
RESULTS OF BRAZING ALLOY WETTING TESTS ON ALUMINA

Brazing Alloy, % Composition							Flow Temp.	Wetting Test Results
Zr	Ti	Be	Fe	V	Cb	Mo		
--	63	--	27	10	--	--	1210 C	Alloy wets Al_20_3 but alloy contains cracks.
48	48	4	--	--	--	--	1060 C	Satisfactory wetting and flowing.
75	--	6	--	--	19	--	1050 C	Satisfactory wetting and flowing.
46	46	4	--	4	--	--	930 C	Satisfactory wetting and flowing.
40	45	--	15	--	--	--	1045 C	Alloy appeared to wet and flow but die not adhere to Lucalox.
4	62	--	26	--	--	8	1200 C	Alloy wetted and flowed but cracked upon cooling.
--	63	--	27	--	--	10	1250 C	Alloy wetted and flowed but cracked upon cooling.
--	68	4	--	28	--	--	1250 C	Wetting and flowing adequate.
80	--	3	17	--	--	--	1000 C	Alloy wetted and flowed but cracks appeared in alloy upon cooling.
67	--	--	4	29	--	--	1300 C	Alloy wetted and flowed but cracked upon cooling.

TABLE 8 (Cont.)
WETTING PROPERTIES AND RESISTANCE TO POTASSIUM OF SOME ACTIVE METALS ON PURE Al_2O_3

Alloy Composition							Approx. Melting Point C	Quality of Wetting on Pure Al_2O_3	Resistance to Potassium: 170 Hr. Exposure at 850 C	Remarks
Ti	Zr	Fe	Cb	Be	V	Mo				
--	67	4	--	--	29	--	1300 C	Poor	Not tested	- -
--	60	--	15	--	25	--	1280 C	Poor	Not tested	- -
48	48	--	--	4	--	--	1050 C	Excellent	Alloy separated from alumina in test. Attack occurred at interface.	Alloy penetrates into and dissolves alumina during brazing.
63	--	--	--	--	27	10	1250 C	Excellent, but cracks occur in brazing alloy upon cooling.	Alloy could be separated from alumina after exposure. Separation occurred at alumina-brazing alloy interface.	- -
63	--	27	--	--	10	--	1280 C	Excellent, but alloy contained may fine cracks and large voids.	Test capsule leaked. Test to be repeated.	- -
68	--	--	--	4	28	--	1250 C	Excellent, but Al_2O_3 cracked under brazing alloy.	Joint intact after exposure but could be removed with some difficulty. Fracture occurrod in crack already present before exposure.	This alloy shows some promise, but Lucalox disk cracked when joined to tantalum tubo with this alloy.

TABLE 8 (Cont.)
WETTING PROPERTIES AND RESISTANCE TO POTASSIUM OF SOME ACTIVE METALS ON PURE Al_2O_3

Alloy Composition							Approx. Melting Point C	Quality of Wetting on Pure Al_2O_3	Resistance to Potassium: 170 Hr. Exposure at 850 C	Remarks
Ti	Zr	Fe	Cb	Be	V	Mo				
45	40	15	--	--	--	--	1050 C	Poor	Not tested	- -
--	75	--	19	6	--	--	1050 C	Excellent	Brazing alloy and tantalum separated from Lucalox in test.	Some columnar grains at interface.
46	46	--	--	4	4	--	1000 C	Excellent, but crack occurred in Al_2O_3 under brazing alloy.	Not tested.	
62	4	26	--	--	--	8	1200 C	Alloy wet, but hair-line cracks occured in brazing alloy during cooling.	Alloy separated from Al_2O_3 at interface.	- -
--	95	--	--	5	--	--	980 C	Excellent wetting.	Alloy separated from Al_2O_3 at interface.	Several leak tight Lucalox disk to tantalum tube joints have been made. These are to be tested in potassium and mercury.
74	--	--	--	--	26	--	---	Excellent	Very little attack on bulk alloy; however, joint parted easily after exposure.	Alloy appears to provide superficial wetting but joint has little strength.

TABLE 8 (Cont.)
WETTING PROPERTIES AND RESISTANCE TO POTASSIUM OF SOME ACTIVE METALS ON PURE Al_2O_3

Alloy Composition							Approx. Melting Point C	Quality of Wetting on Pure Al_2O_3	Resistance to Potassium: 170 Hr. Exposure at 850 C	Remarks
Ti	Zr	Fe	Cb	Be	V	Mo				
62.5	--	--	--	--	37.5	--	---	Excellent	Significant attack on bulk alloy.	No additional joints made due to gross attach on alloy.

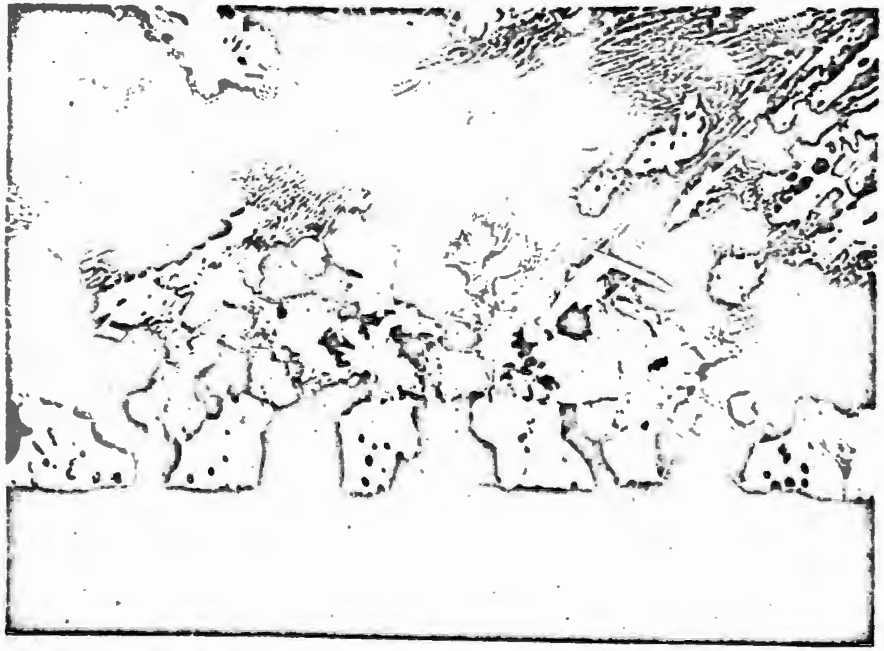


Figure 32. Interface Between Brazing Alloy and Lucalox

Columnar grains at interface may indicate solution of Lucalox in brazing alloy. Joints have adequate strength but only poor to fair resistance to potassium at 850 C

Figure 33. Micrograph (250X) of Interface Between Lucalox and 95% Zr-5% Be Brazing Alloy

Figure 34. Micrograph (100X) of Brazing Alloy Interface Exhibiting Bonded Structure

The brazing alloy (67% Zr-29% V-4% Fe) exhibits a bonded structure, which probably consists of a solution of Al_2O_3 in the brazing alloy. White light and unetched.

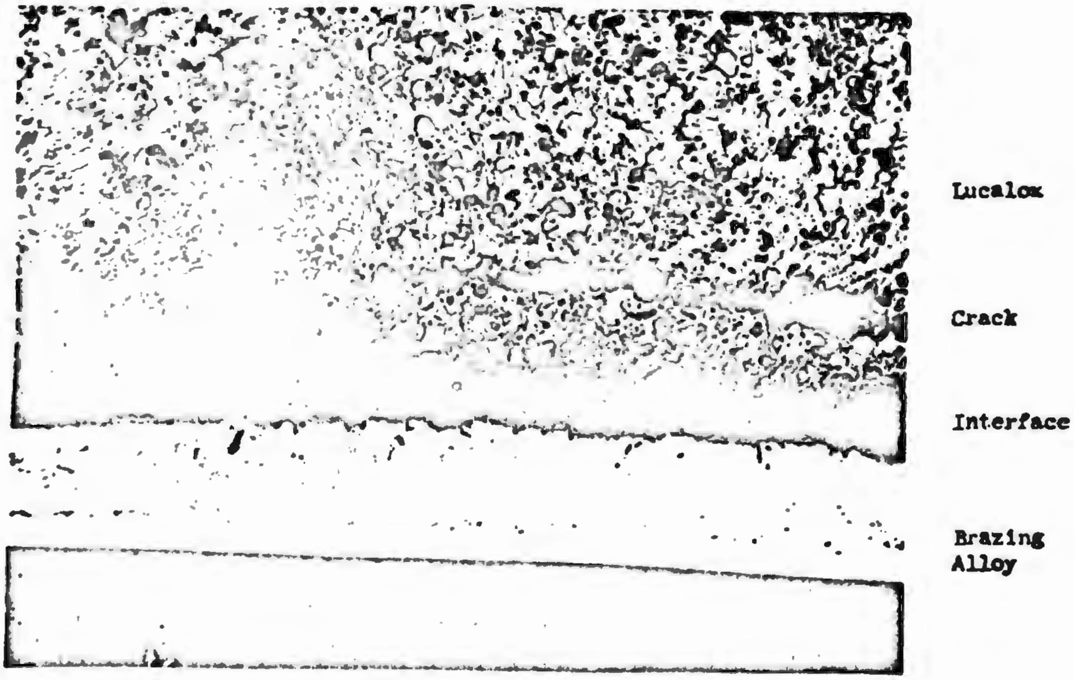


Figure 35. Micrograph (100X) of Lucalox Specimen Showing Crack Formed When Brazing Alloy Cooled

This specimen was wetted with 48% Beryllium-48% Titanium-4% Beryllium. Then cracking behavior was observed with several allows, and the cracks are probably caused by solidification shrinkage and difference in the thermal coefficient of expansion.

(1) 95% zirconium-5% beryllium. Six specimens consisting of "T joints" between tantalum and Lucalox were tested. Two or these showed some adhesion but could be separated after potassium exposure.

(2) 63% titanium-27% iron-10% molybdenum. The brazing alloy did not separate from the alumina during exposure, but could be separated from the main body of alumina after test. Fracture occurred at the interface.

(3) 68% titanium-28% vanadium-4% beryllium. The brazing alloy did not separate during potassium exposure, and the brazing alloy could be separated from the Lucalox but only with difficulty. Fracture occurred in the Lucalox under the brazing alloy. However, cracks are formed in the alumina wetted with this alloy so the crack observed after exposure probably occurred in the brazing cycle.

4.4.2 Electrical Test Capsule Preparation

Lucalox to tantalum tube and sapphire to tantalum tube seals were made. The ceramic was 0.5 inch O.D. 1/16 and 1/8 inch thick, with 0.030 inch hole in the center. These were brazed to the tantalum tubes with 95% Zr - 5% Be alloy. The tubes were 0.5 inch O.D., so that they had to be flared out to obtain a satisfactory slip-fit of the ceramic disk. The wall thickness of the tantalum was 0.020 inch. A 0.020 inch Ta wire was brazed into the center hole for lead-in.

Out of nine attempts, four brazed units were satisfactory; i.e., they were vacuum tight on thermal cycling to 850 C. Some tube joints were also made with 68% titanium, 4% beryllium, 28% vanadium, but the Lucalox disks cracked in each tube joint made.

Two tubes were prepared for use in electrical tests during potassium exposure. These consisted of a tantalum tube brazed to a stainless steel tube with a nickel base alloy (Nicrobraz 130) in vacuum. Both joints were found to be leak tight. Later, sapphire disks were brazed onto the tantalum portion of the tube and both joints were leak tight, but the sapphire disks cracked during pre-exposure electrical tests in argon at 850 C. Our experience indicates that the single crystal sapphire disks crack more easily than the polycrystalline Lucalox in such tests.

Attempts at constructing Lucalox to Ta-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 ($\sim$ 1100 C) and thinner fillet results in crack-free seals with good bond.

Lucalox to Ta-tube seals, using Mo-Mn-metallized Lucalox disks in conjunction with Nicrobraze 130 alloy, were also unsuccessful. Prospects for success here was poor in view of the fact that the Mo-Mn metallizing detached from the Lucalox when the brazing alloy was fused onto it.

4.4.3 Seal Formation Using Glasses

Attempts at constructing Lucalox to Ta-tube seals for Hg vapor tests with aluminum silicate glass were unsuccessful, due to unfamiliarity with process variables during the brief period spent on this type of seal. Since the brazing alloys for the K vapor exposure are resistant to Hg vapor, no further work was done on this glass seal.

Work by another group on a Westinghouse funded program resulted in an alumina-calcia glass (fires at 1500 C) that produces an alumina to niobium joint that is not affected by 172 hours exposure to K vapor at 850 C. The only successful joints made to date consist of niobium end caps banded to the end of an alumina tube. The high firing temperature of the glass and the need to use the alumina tube-niobium disk configuration prevented immediate use of the development in the present program.

The cracks which appear either in the brazing alloy or in the Lucalox may be attributed to the lack of ductility of the alloy during cooling; or it may be due to hot tearing because of low melting ranges as the alloy cools, or to the difference in thermal expansion when cracks occur in the alumina.

The active metals are reported to wet alumina by a chemical reaction between the alumina and the active metal oxides. However, the typical layer of this reaction product cannot be definitely identified in the micrographs. The microstructure of the various active alloys at the alumina interface varies; some have a rather columnar structure and others have a banded structure. The latter structure may be a solution effect of the alumina partially dissolved in the brazing alloys.

The results have shown that most of the titanium and zirconium alloys tested will wet alumina. Leak tight joints between tantalum and alumina may be made with the zirconium-beryllium alloy. Potassium exposure tests on small "T joints" indicate that none of the alloys have good resistance to potassium vapor. However, joints with long corrosion paths have not been tested. It is thought that such joints electroplated with nickel may exhibit sufficient resistance to potassium to permit the tests to be made. A redesign of the joint configuration and a change in brazing technique could minimize cracking of the ceramic disks. Also, the specimens coated with silica-free molybdenum-manganese are expected to provide adequate resistance to potassium. Initial trials of diffusion bonding indicate that some success may be obtained by this approach. Combined mechanical and metallurgical seals using stainless steel "O" rings and a top braze may also provide a leak tight seal.

4.5 Wire Coatings

4.5.1 Materials and Coating Methods Survey

A survey of the available literature resulted in a list of 41 candidate materials that are good electrical insulators at temperatures above 100 F. These data resulting from the survey are presented in Table 9. The data indicates considerable variation in Te values for some materials. This is primarily due to variations in impurities content. A comparison using manufacturers data when available was made to prevent duplication and unnecessary testing. Single crystal and high purity polycrystalline oxides were obtained from various suppliers who were making these materials on a research or development scale.

A survey of coating methods was made and a number of techniques were uncovered for coating wire that offered promise. These are described in detail in the sections that follow. The presence of the copper or silver core in the candidate conductors limited the maximum processing temperatures in any of the coating methods to about 1000 C.

4.5.2 Fusion Coatings

Fusion coatings using high purity alumina, magnesia, or beryllia would require use of processing temperatures much in excess of the 1000 C limitation set by the conductor.

TABLE 9
INSULATING MATERIALS WITH Te* VALUES ABOVE 1000 F

	Material	Trade Name or Designation	Supplier	Te Value in °F
1.	Porcelain	BV600	Gen. Ceramics	1112
2.	Zirconium Oxide	Alsimag 508	Amer. Lava	1130
3.	Aluminum Silicate	Lava Grade A	Amer. Lava	1148
4.	Zirconium Oxide	Alsimag 550	Amer. Lava	1157
5.	Steatite	#13889	Frenchtown Porcelain	1170
6.	Porcelain	BV582	Gen. Ceramics	1202
7.	Alumina	Alsimag 491	Amer. Lava	1238
8.	Zircon	#3569	Frenchtown Porcelain	1251
9.	Zircon	Alsimag 504	Amer. Lava	1292
10.	Cordierite	#5301	Frenchtown Porcelain	1369
11.	Steatite	Alsimag 196	Amer. Lava	1382
12.	Cordierite	Alsimag 202	Amer. Lava	1436
13.	Alumina	Alumicox #4462	Frenchtown Porcelain	1472
14.	Alumina	ADL210	Gen. Ceramics	1472
15.	Magnesium Silicate	Lava 1136	Amer. Lava	1490
16.	Steatite	Alsimag 228	Amer. Lava	1508
17.	Alumina	Alsimag 393	Amer. Lava	1535
18.	Steatite	Alsimag 197	Amer. Lava	1544
19.	Alumina	Alsimag 491	Amer. Lava	1544
20.	Steatite	BN3942	Gen. Ceramics	1562
21.	Zircon	M-81-A	Gen. Ceramics	1562
22.	Alumina	AB-2	Coore	1562
23.	Zircon	Alsimag 475	Amer. Lava	1598
24.	Alumina	AL-100	Coore	1679
25.	Alumina	Alite 212	U. S. Stoneware	1787
26.	Thoria	Thorox	Nat. Beryllia	1830
27.	Magnesium Silicate	BN3055	Gen. Ceramics	1832

*Te is the temperature at which a material has an insulation resistance value of one megohm-cm.

TABLE 9 (Cont.)
INSULATING MATERIALS WITH Te* VALUES ABOVE 1000 F

	Material	Trade Name or Designation	Supplier	Te Value in °F
28.	Forsterite	BN3054	Gen. Ceramics	1832
29.	Alumina	AL-300	Western Gold & Platinum	1832
30.	Forsterite	Alsimag 243	Amer. Lava	1832
31.	Magnesium Silicate	Alsimag 222	Amer. Lava	1832
32.	Alumina	1009	Western Gold & Platinum	2012
33.	Alumina	AL-200	Coore	2138
34.	Magnesia	Alsimag 555	Amer. Lava	2192
35.	Alumina	Alox	Nat. Beryllia	2250
36.	Beryllia	Berlox	Nat. Beryllia	2400
37.	Strontium Zirconate		Zirconium Corp.	1870
38.	Alumina + Yttria		Zirconium Corp.	--
39.	Magnesia (Single Crystal)		Muscle Shoals Electro Chem. Co.	--
40.	Boron Nitride		Carborundum Co.	--
41.	Alumina (Single Crystal)		Linde	--

*Te is the temperature at which a material has an insulation resistance value of one megohm-cm.

The fusion of very finely divided oxides is possible at much lower temperature than with the same but coarser form of the oxide. The addition of very small amounts of silica have been shown to materially reduce this lower temperature even further. Although silica is generally considered detrimental to resistance to potassium vapor, Cowan of the Los Alamos Scientific Lab. (7) reported that up to 1% silica in alumina was tolerable in cesium vapor at 2200 F. Since coating compositions of finely divided oxides could readily be continuously fused onto conductors using a tube furnace or RF heating, this approach was looked at. The initial fusion coating trials were made using either collodial particles or particles obtained from decomposition of metallo-organics. Table 10 contains a listing of the early coatings, their adherence and electric strength obtained using a Slaughter Company Leakage Tester Model 103/105. A mixture of magnesia and alumina was coated on Oxalloy 28 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 coating properties of the mixture were very good. A thin uniform coating was produced on short lengths of conductor dipped in the slurry. The adhesion of the fired coating was good; however, bending the coated wire after cooling caused the coating to come off. The electric strength of the coated conductors ranged from 250 to 650 volts (conductor to ground). This coating, however, was found to contain a high percentage of titania and therefore would not exhibit the desired electrical properties at 850 C. A silica free fusion coating has not been obtained even at temperatures in excess of the maximum temperature allowable for the conductor material.

Very brief exposures of the various coatings investigated to 1400 C was attempted to obtain fusion but without success. Even though this temperature was 450 C above the allowable conductor temperature, the short duration of the exposure allowed the coating to reach a high temperature without the conductor exceeding its maximum temperature.

Very good coatings have been obtained using fine alumina in a collodial zirconia solution. The coating, when dried and fired to 1000 C, is adherent, uniform in thickness and will not rub off. This coating has been successfully applied to stainless steel, Inconel and nickel substrates. Application to stainless steel has resulted in the coating popping off or having blisters in certain areas after firing at 1000 C. Microscopic examination of the fired coating in the blistered areas has shown the formation of an oxide coating on the stainless steel causing this blister effect. Firing in an inert atmosphere eliminated this problem.

TABLE 10
FUSION COATING OF CONDUCTORS

Composition	Adherence	Coating Fused	Electric Strength - Volts (at 2.5 MA Current Leakage)
1. Colloidal Alumina + Colloidal Silica	Poor	No	---
2. Same + addn. dip in Colloidal Silica	Good	No	250
3. Colloidal Alumina - dried + Colloidal Silica	Good	Yes	200
4. Colloidal Silica	Good	Yes	50
5. Magnesium Metholate + Alumina Ratio 5-1	Good (Cracked)	No	250
6. Same Ratio 5-2	Good	No	250
7. Same Ratio 5-3 + Colloidal Silica	Very Good	Yes	650
8. Same Ratio 5-3-1 Ethyl Silicate	Fair	Yes	200

Subsequent overcoating of the alumina-zirconia coating with ammonium zirconyl carbonate has produced a very smooth, abrasion resistant surface. Unfortunately, this overcoating on refiring produces enough shrinkage to form cracks in the coating.

The alumina-zirconia fusion coating on Oxalloy 28 (Sample PK-9) completely disintegrated during a 172 hour exposure to potassium vapor at 850 C. Since the high purity alumina and zirconia are resistant to the environment, it is felt that no fusion bond had formed in the coating, only an amorphous interface that was readily attacked by the potassium vapor. Since the fusion coating method did not appear to be suitable for providing the dense, highly crystalline coating of ultra pure material necessary for adequate resistance to attack by potassium vapor, work on this approach was terminated.

4.5.3 Formation of Boron Nitride Coating

Thermal decomposition of B trichloroborazole in the vapor phase with deposition of boron nitride was investigated. Gaseous HCl is the other product formed. The deposition trials were carried out in a Vycor tube with radio frequency heating used to heat the substrate to be coated and resistance heaters to vaporize the B trichloroborazole. In trials where a carrier gas flow was used, the substrate was located downstream of the vapor source. In continuously pumped systems, the substrate was between the vapor source and the vacuum source. Ten initial coating trials were made. Eight are listed below.

(1) A tungsten rod 3/16" in diameter and 2" long was sealed in vacuum together with several grams of $Cl_3B_3N_3H_3$ in quartz tube of about 23 cc volume. The materials were positioned at opposite ends of the tube and heated. The rod was taken to 1500 C and the trichloroborazole to 113 C (vapor pressure of $Cl_3B_3N_3H_3$ = 61.1 mm). (8) A heavy white greyish non-conducting film was formed, which adhered to the rod well.

(2) A coil of tungsten wire was heated to 1475 C and the $B_3Cl_3N_3H_3$ at 75 C (vapor pressure between 6.9 to 12.6 mm. (8) 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 36).

(3) Several tests were made on stainless steel sheathed copper wire coils to determine the feasibility of coating the wire with BN. The wire coils were heated with the 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.

(4) 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).$^{(8)}$ Total time of run was 1.5 hours. The wire was well coated with a semi-transparent white coating which was an electrical insulation. This film was comparatively strong mechanically, but it could be flaked off by applying pressure with the fingers.

(5) A graphite rod 1/4" in diameter was fired as a substrate at 1475 C. The trichloroborazole was heated at 40 C (~0.6 mm pressure).$^{(8)}$ 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. Nothing flaked off or was lost.

(6) Platinum cylinders, 3/8" in diameter, 1" long, and with walls 0.001" thick were used as substrates. The cylinders were fired at 1300 C with a maximum pressure of $Cl_3B_3N_3H_3$ of about 3.7 mm.$^{(10)}$ The first cylinder was fired for three hours under these conditions. The interior and exterior of the tube were 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

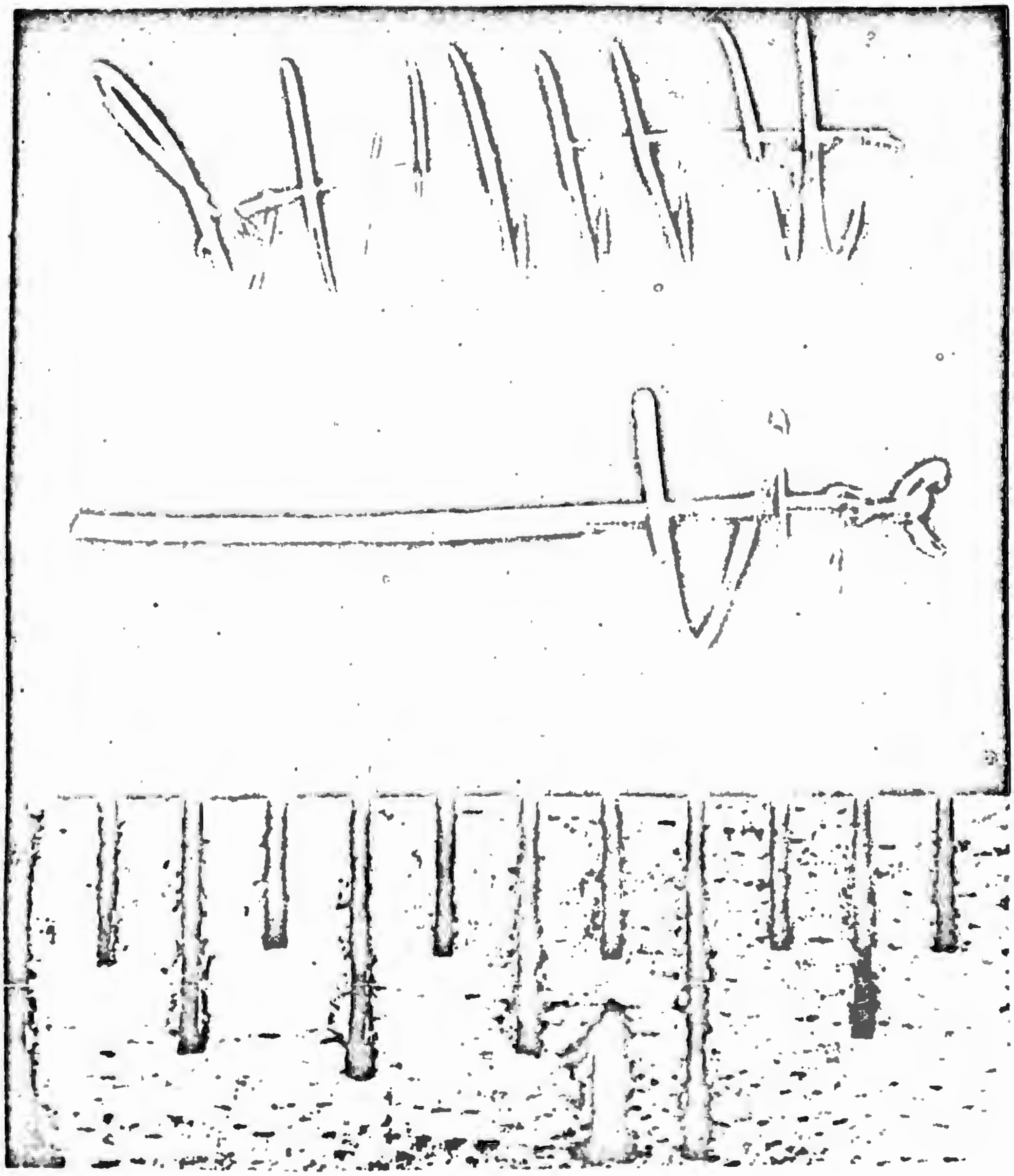


Figure 36. Boron Nitride Deposit on Tungsten Wire

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.

(7) 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 fired at 1150 C in vacuum with the "B" trichloroborazole temperature at 50 C. After a 25 minute run, the RF generator cut out. The surface of the slab was a light tan line with a few sparse crystalline white spots, small in size, 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 film, which flaked off, was of insulating character. The slab itself, colored in various shades of brown, was conducting.

(8) Twenty mil tungsten wire, wound in a shorted 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 six hour run was made with substrate heated to 1115 C and with the trichloroborazole heated to 60 C. The coil was again vacuum cooled. The film began to flake and pop a short time after exposure to air. 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.

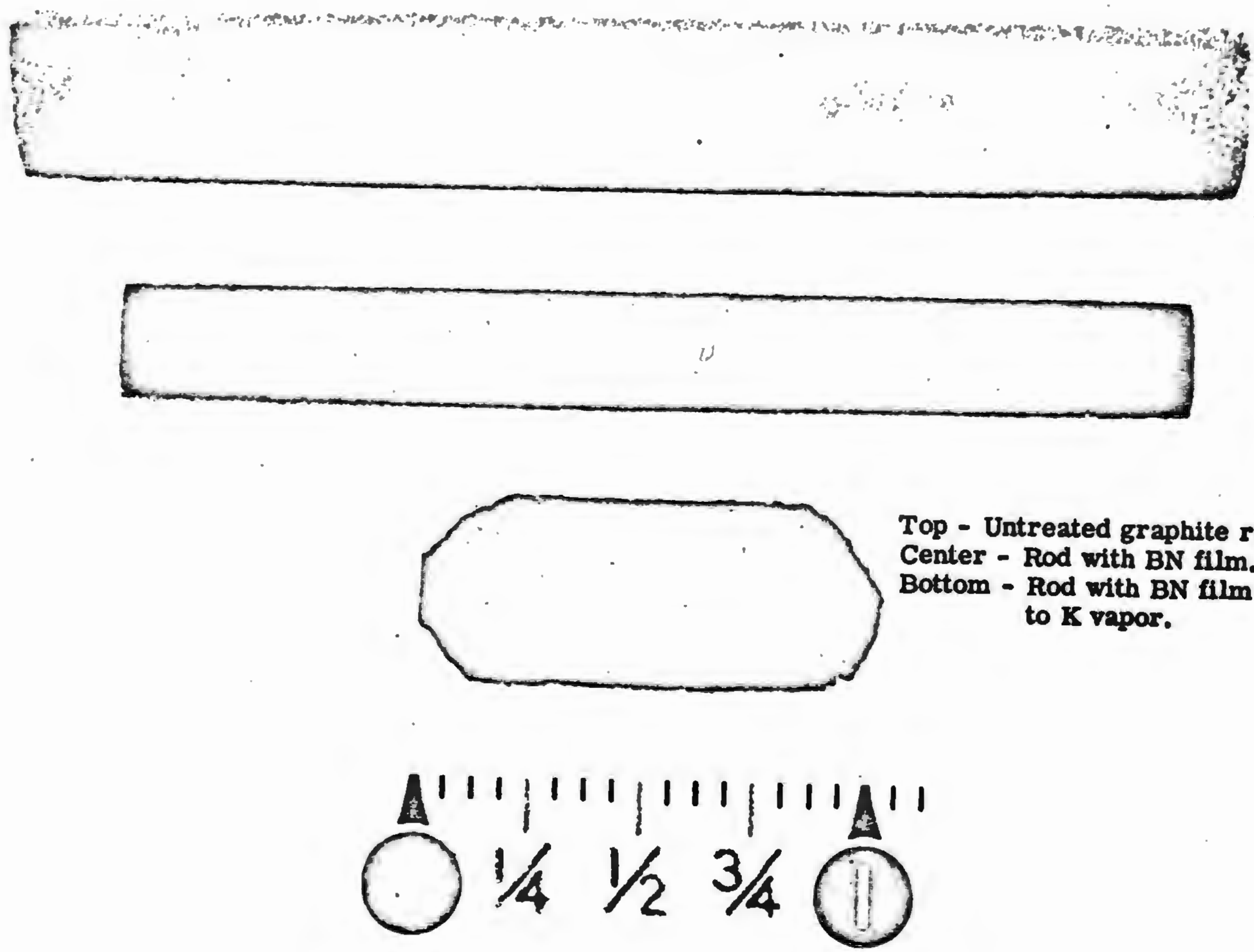
Work was directed at getting continuous and hole-free boron nitride coatings on the substrates, stainless steel sheathed copper and graphite rod. Only the rod and wire samples which showed the most continuous coatings were used in the K vapor tests.

The reason for the selection of graphite as a substrate was that it is fairly compatible with the BN film and that it is highly susceptible to attach by potassium vapor at 850 C. Previous tests showed that graphite rod exposed to the metal vapor was completely reduced to a powder. The condition of a filmed graphite rod at the completion of the K vapor exposure tests would give some insight as to the ability of the film to provide protection against potassium attack.

Results of the exposure of the filmed substrates to potassium vapor at 850 C for 172 hours seem to indicate some degree of resistance to the alkali metal attack.

Figure 37 shows the appearance of several graphite rods. The top rod is untreated, the center rod is filmed with BN but has no other treatment, while the bottom rod (sample RB24-1) had been exposed to K vapor at 850 C for 172 hours. The rod still retains a good portion of its mechanical strength and manifests alkali metal attack predominately at the surface, which has a flaked appearance. After 6 weeks exposure to air, this flaked surface acquired a white grey cast. The rest of the rod remained black in color. This color change might be due to hydrolysis of the BN film remaining on the rod. There was only a slight tendency of the rod to powder. Taking into consideration the fact that the BN coating on the rod was not perfectly continuous and hole free to start with, there is some indication that the film afforded the graphite a measure of protection.

Few deductions can be drawn from the run on stainless steel clad copper wire coil (sample RB371). The stainless steel sheathing appeared intact and had no obvious chemical attack. The film was opaque white to grey in color and is very easy to wipe off the conductor. The film remaining on the coil is nonconducting. Figure 38 shows the coil after exposure to potassium vapor at 850 C for 172 hours. Figure 39 shows a boron nitride coated stainless steel clad copper wire.



Top - Untreated graphite rod.
Center - Rod with BN film.
Bottom - Rod with BN film exposed
to K vapor.

Figure 37. Carbon Rods From BN Forming Work

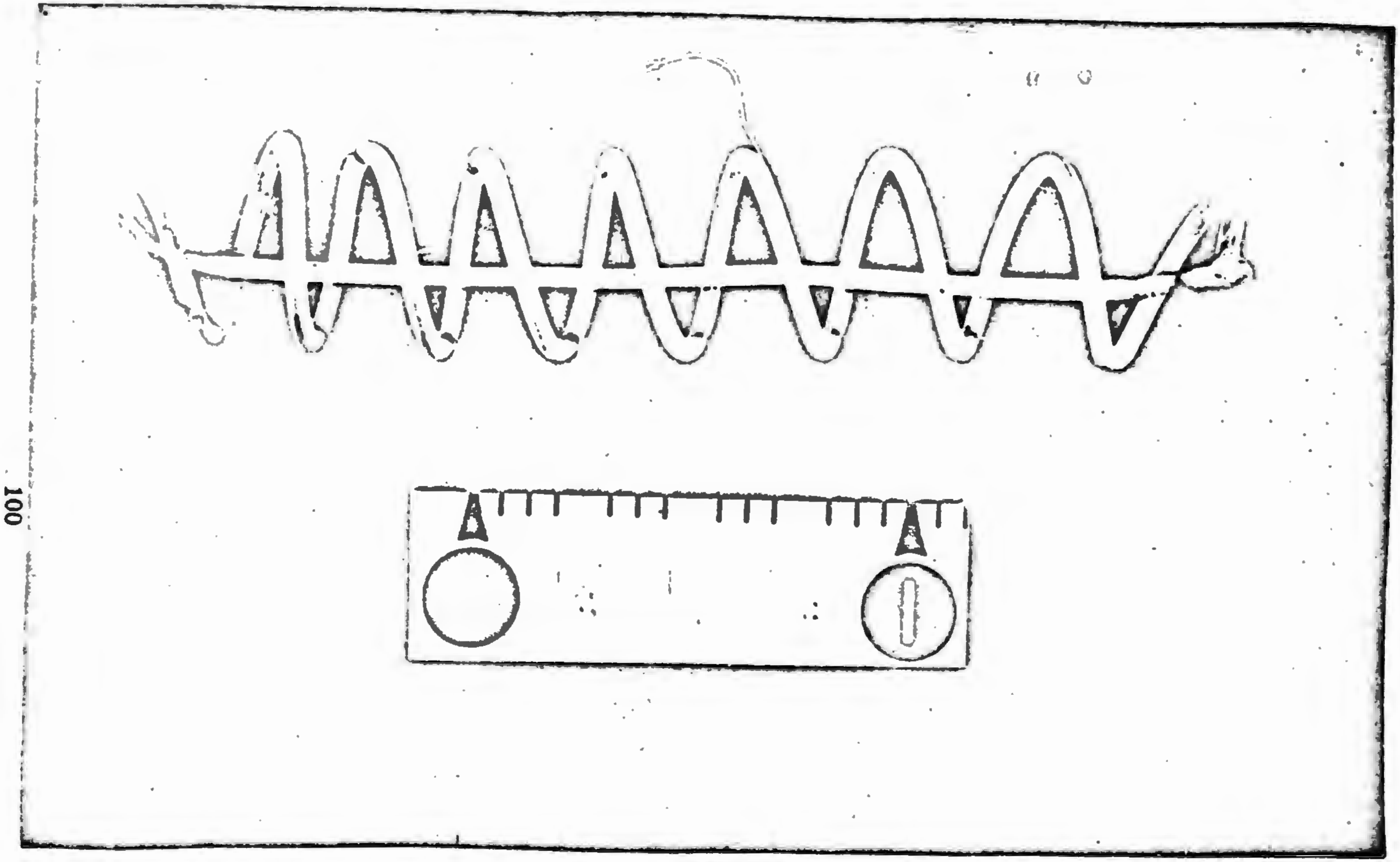


Figure 38. BN Coated Oxalloy 28 Wire After Exposure to K Vapors (RB37-1)

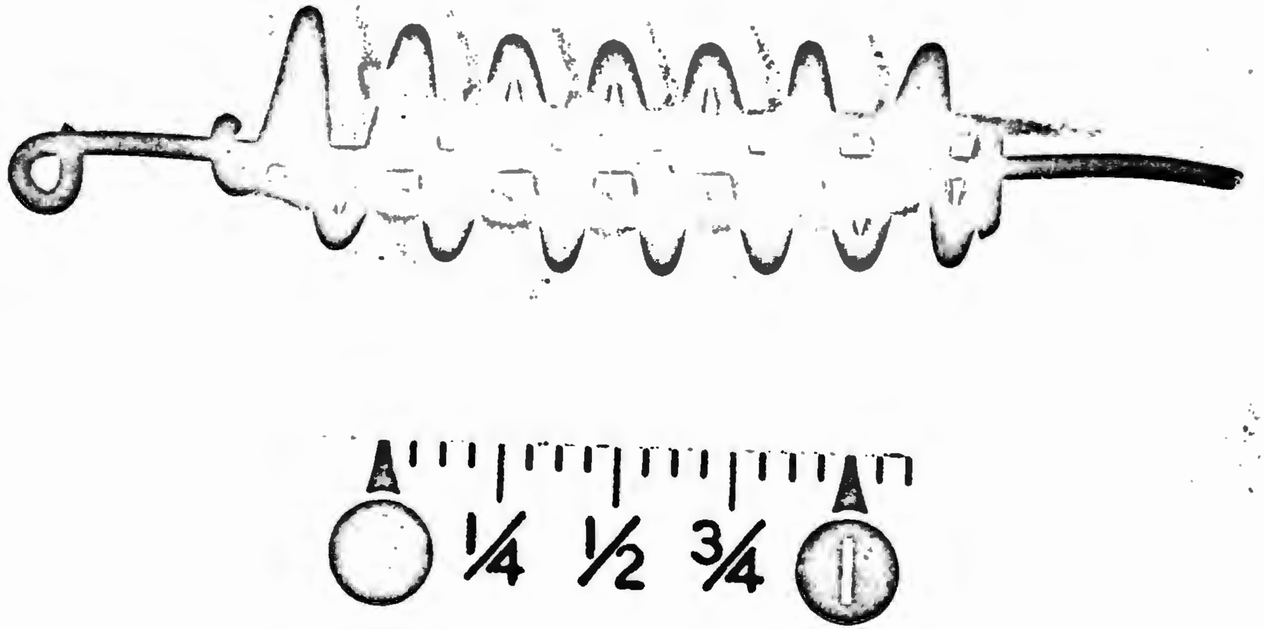


Figure 39. BN Coated Oxalloy 28 Wire

The film, which ranges from transparent to opaque white in samples, is transparent in this case.

X-ray results on the films of some previously run samples have been received. Table 11 lists the samples, substrates and substrate temperatures during the pyrolysis of the trichloroborazole. The X-ray diffraction values for these samples are listed in Table 12, along with the d values of BN and graphite from the ASTM index. All patterns were taken (with the exception of S13M) in 114.6 mm Debye Scherrer powder cameras using nickel filtered copper radiation. Sample RB241-B was a piece of the film from RB24-1-A which was given an additional 3 hours heating in air at 980 C. Sample R53R-2 was a fluffy white deposit on the boat holding the tungsten wire coil (sample R53R-1). The boat was relatively cool compared to the wire coil.

X-ray diffraction patterns were obtained for the coatings. These patterns are shown in Figures 40 through 44.

The samples are of a low order of crystallinity since bands were formed instead of sharp lines. The only exception is sample R53R-2 which is amorphous. The absence of impurity lines does not exclude the presence of impurities but merely indicates they are not present in a measurable degree or that they are masked by the broad sample lines. Except for line width and sharpness, all patterns are identical except R53R2 which is amorphous. Because of the similarity in structures of BN and graphite, all samples with graphite substrate should be interpreted with caution. Sample S13M was identified as hexagonal boron nitride. These X-ray results agree with those described by Patterson.(9) The iron oxides appearing in sample RB11X1 are from the momentary failure of the vacuum system.

Infrared spectra of several samples from different substrates were secured. Hexagonal boron nitride has absorption peaks at 7.2 and 12.2 microns. The spectra from the samples can be divided into 3 groups.

A) Samples R291 (platinum substrate at 1300 C), R440-1 (Inconel substrate at 1155 C), RB271D, and RB271C gave a very broad maximum in the 8 and 9 micron region and a broad absorption peak at 12.5 microns. Samples RB27-1-D

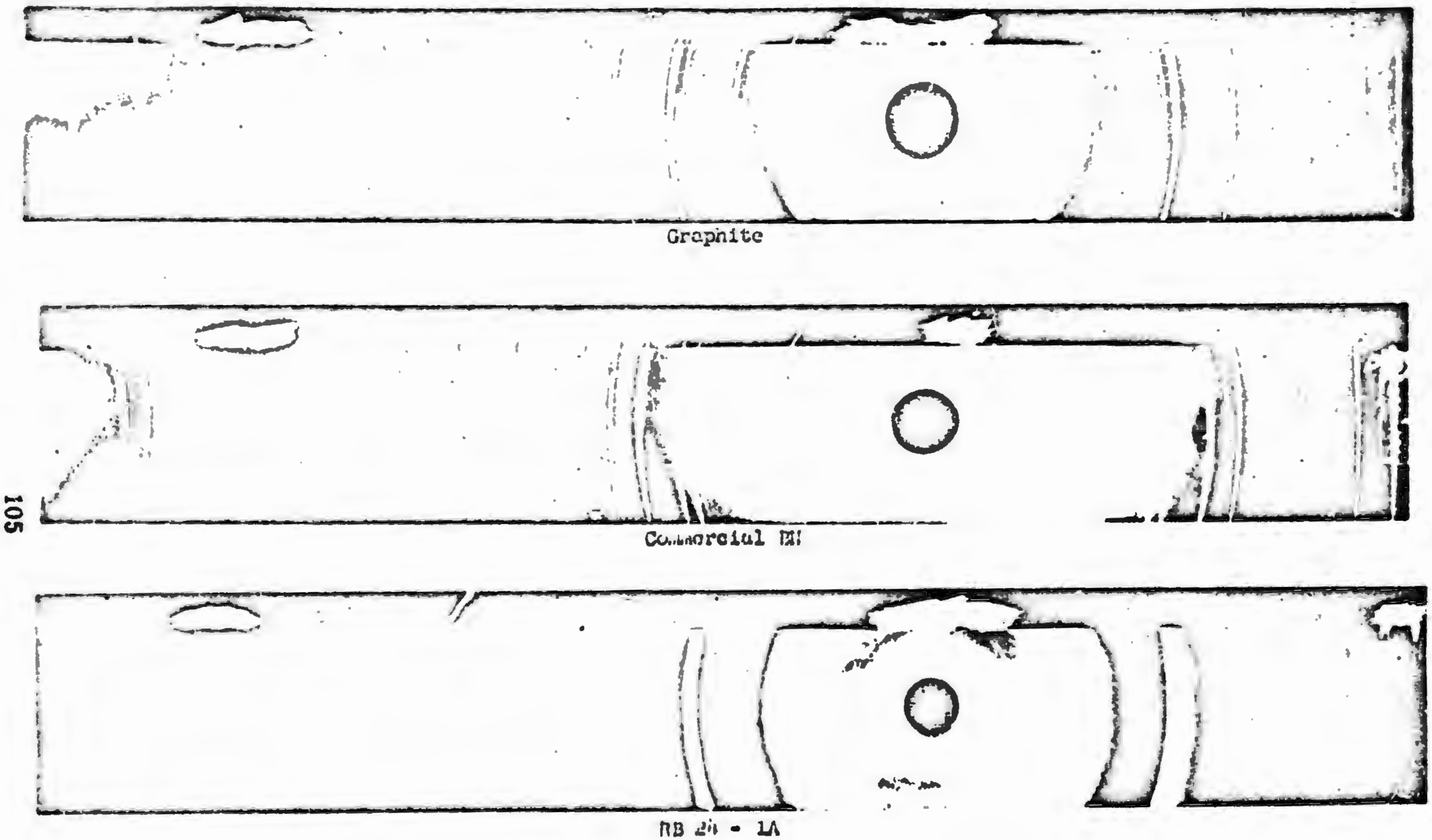
TABLE 11
SAMPLE SUBSTRATES AND TEMPERATURES USED TO FORM BN COATINGS

Sample	Substrate	Substrate Temperature (°C)
RB241A	graphite	1445
RB18-1	platinum	1000
R500-1	stainless steel clad Cu	925
RB24-1	graphite	1445
R4401	inconel	1155
RB24-1B	graphite	annealed at 980 C for 3 hrs. in air
R53R-2	(boat deposit)	
RB11X-1	stainless steel rod	1005
R53R-1	tungsten wire	1950
RB27-1	graphite	1375
R29I-1	platinum cylinder	1300
S13M	platinum wire coil	1375

TABLE 12
X-RAY DATA FOR FILM DEPOSITS*

Sample	d Values from X-Ray Data							
BN (ASTM)	3. 31	2. 16	2. 05	1. 81	1. 66	1. 25	1. 17	1. 00
Graphite (ASTM)	3. 35	2. 12	2. 03	--	1. 67	1. 225	1. 15	.98
RB241A	3. 40B**	2. 12B	--	--	1. 70B	1. 23B	--	--
RB18-1	3. 40B	2. 12B	--	--	--	1. 24B	1. 16B	--
R50Q-1	3. 45B	2. 14B	--	--	1. 72B	1. 24B	--	--
RB24-1	3. 50B	2. 12B	--	--	1. 70B	1. 23B	--	--
R440-1	3. 40B	2. 11B	--	--	1. 72B	1. 23B	--	--
RB241B	3. 40B	2. 10B	--	--	--	1. 22B	--	--
R53R-2				- - - - - AMOSPHOUS - - - - -				
RB11X-1	3. 40B	2. 11B	--	--	--	1. 22B	--	plus Fe_2O_3 and Fe_3O_4
R53R-1	3. 40B	2. 12B	--	--	1. 72B	1. 23B	1. 17B	
RB27-1	3. 40B	2. 10B	--	--	--	1. 23B	--	
R29I-1	3. 25B	2. 10B	--	--	1. 70B	1. 23B	--	

*All patterns taken in 114-6 mm Debye Scherrer powder cameras using Nickel filtered copper radiation.

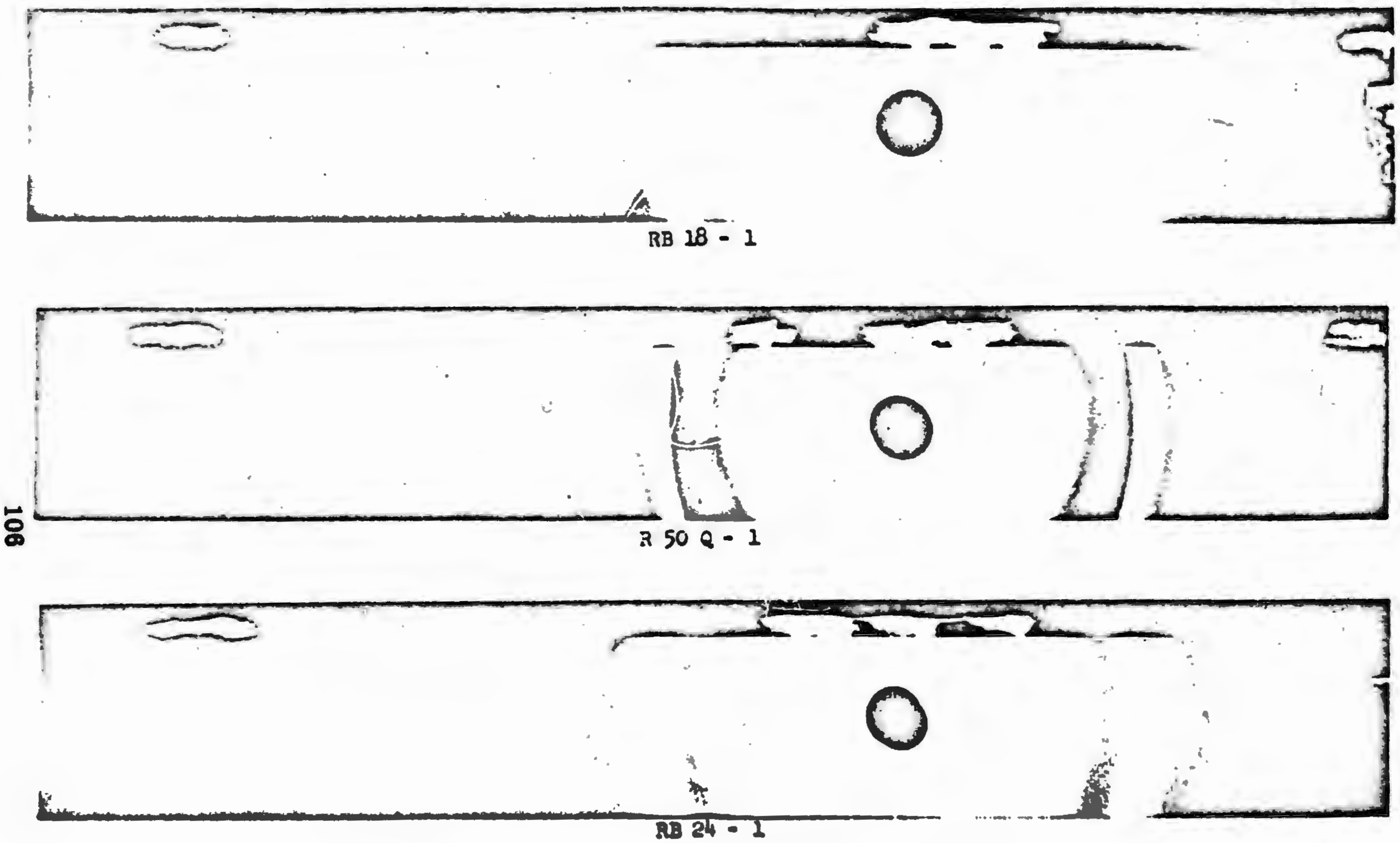


Graphite

Commercial III

RB 24 - 1A

Figure 40. X-ray Diffraction Patterns for Deposited Films


RB 18 - 1

R 50 Q - 1

RB 24 - 1

Figure 41. X-ray Diffraction Patterns for Deposited Films

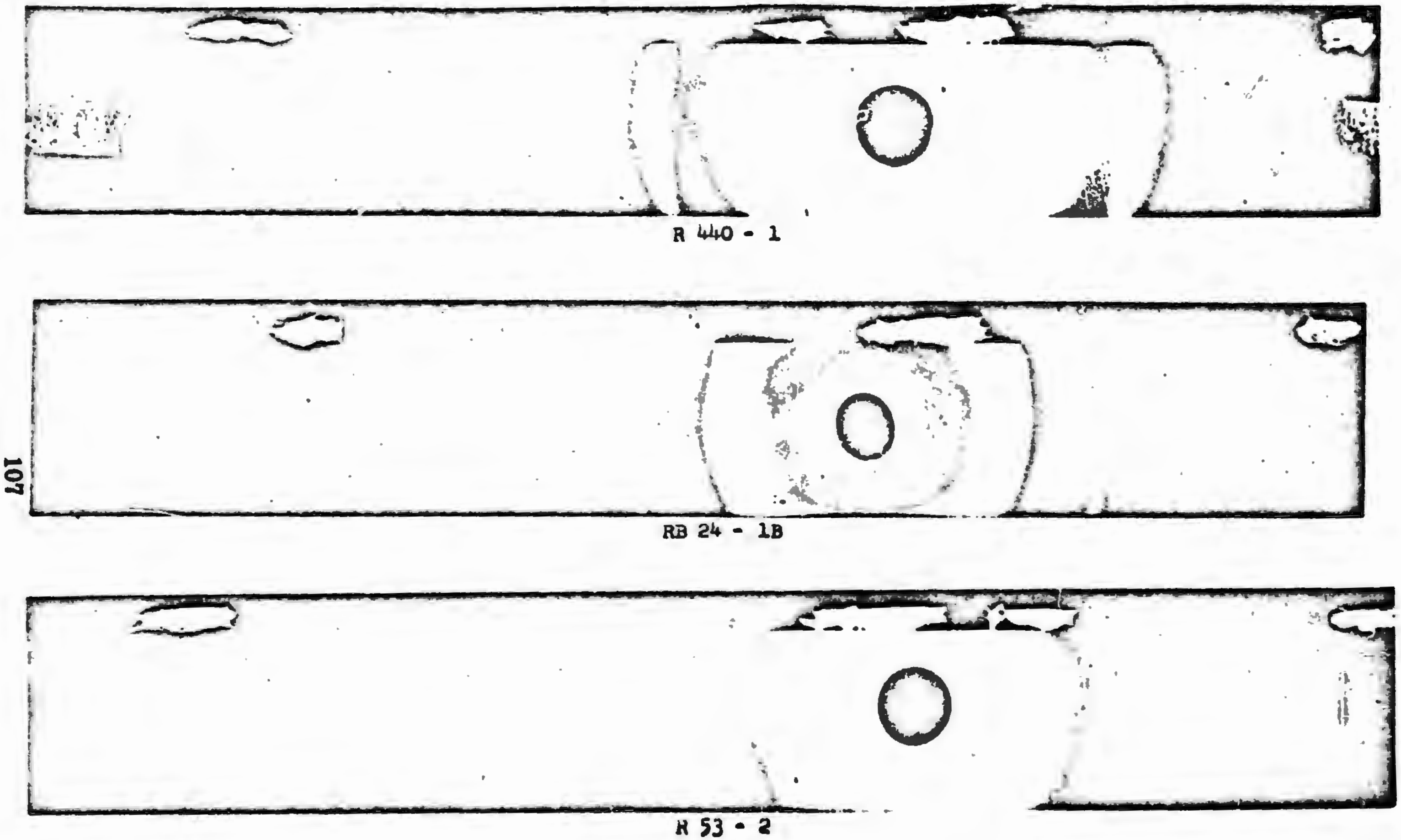
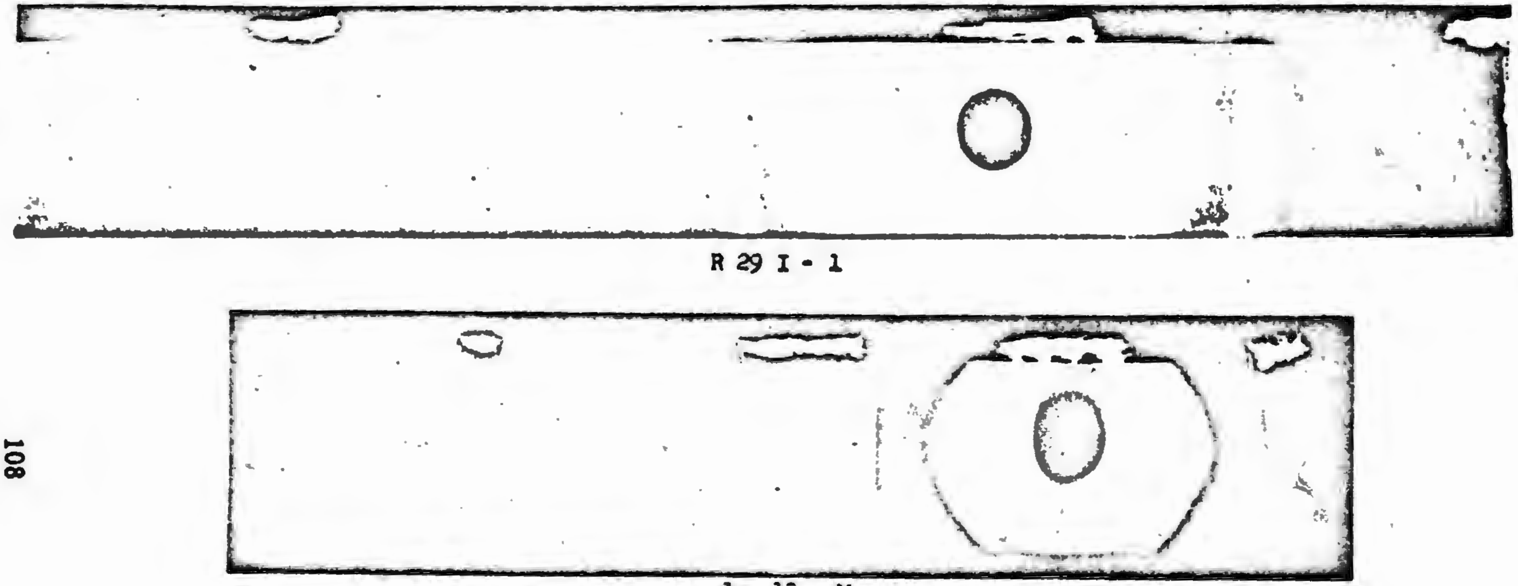
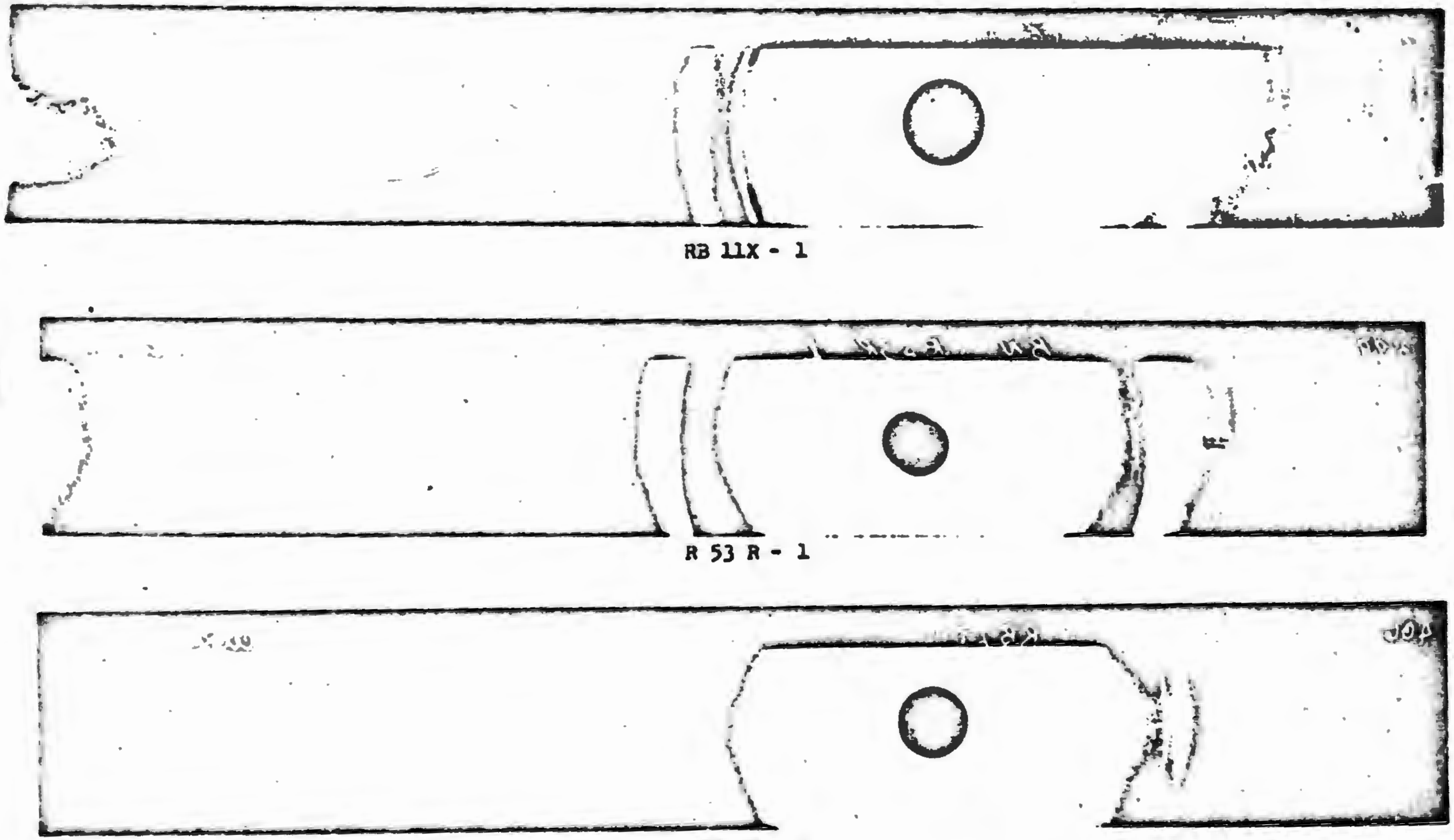


Figure 42. X-ray Diffraction Patterns for Deposited Films


R 29 I - 1

S - 13 - M

Figure 43. X-ray Diffraction Patterns for Deposited Films



RB 11X - 1

R 53 R - 1

RB 27 - 1

Figure 44. X-Ray Diffraction Patterns for Deposited Films

and RB27-1-C were fragments of a spalled film obtained by heating a graphite rod substrate at 1375 C in trichloroborazole vapors, cooling, removing the rod, rotating and revolving the rod 180° and reheating in $Cl_3B_3N_3H_3$ vapors. The secondary coating flaked off the rod and was used for samples. It should be noted that this coating was formed at a lower temperature than indicated at the surface of the rod. RB27-1-C was submitted with no further treatment. RB27-1-D was heated in air for 3 hours at 980 C. The infrared spectra data on the above samples are shown in Figures 44 and 45.

B) Samples R50Q-1 (film from tungsten were substrate at 1450 C), S9F (tungsten rod substrate at 1050 C and S53R-2) (a powdery white deposit in front of a boat containing a tungsten substrate at 1950 C) gave an absorption peak at 7.2 microns and a broad absorption peak at 12.5 microns. Infrared spectra data on these samples are shown in Figures 45, 46 and 47.

C) Sample S53R1 (deposit on a tungsten wire coil substrate at 1950 C) has absorption peaks at 7.2 and 12.2 microns and a broad absorption peak at 12.5 microns. Infrared spectra data are shown in Figure 47.

The infrared spectra indicate the samples to be boron nitride but of varying degrees of crystallinity. Sample S53R1 is the only one having hexagonal boron nitride to an appreciable degree according to the infrared results. The higher temperatures of the substrate tend to give boron nitride of a more hexagonal crystalline nature. This is borne out by the X-ray data which shows a slight sharpening of the lines with increasing substrate temperature.

The majority of the BN filmed substrates gave off an odor of ammonia after being exposed to air for some time. There is a basic reaction with moist litnus paper held over the mouth of the vials. Poaszus (10) reported that on extensive boiling with water or acid solutions, boron nitride hydrolyzes to NH_3 and boric acid. Furthermore, it has been reported in the literature that the chemical stability of BN is dependent on the temperature at which it is produced or later heated. Boron nitride produced at 130 C is easily decomposed by moisture (11),

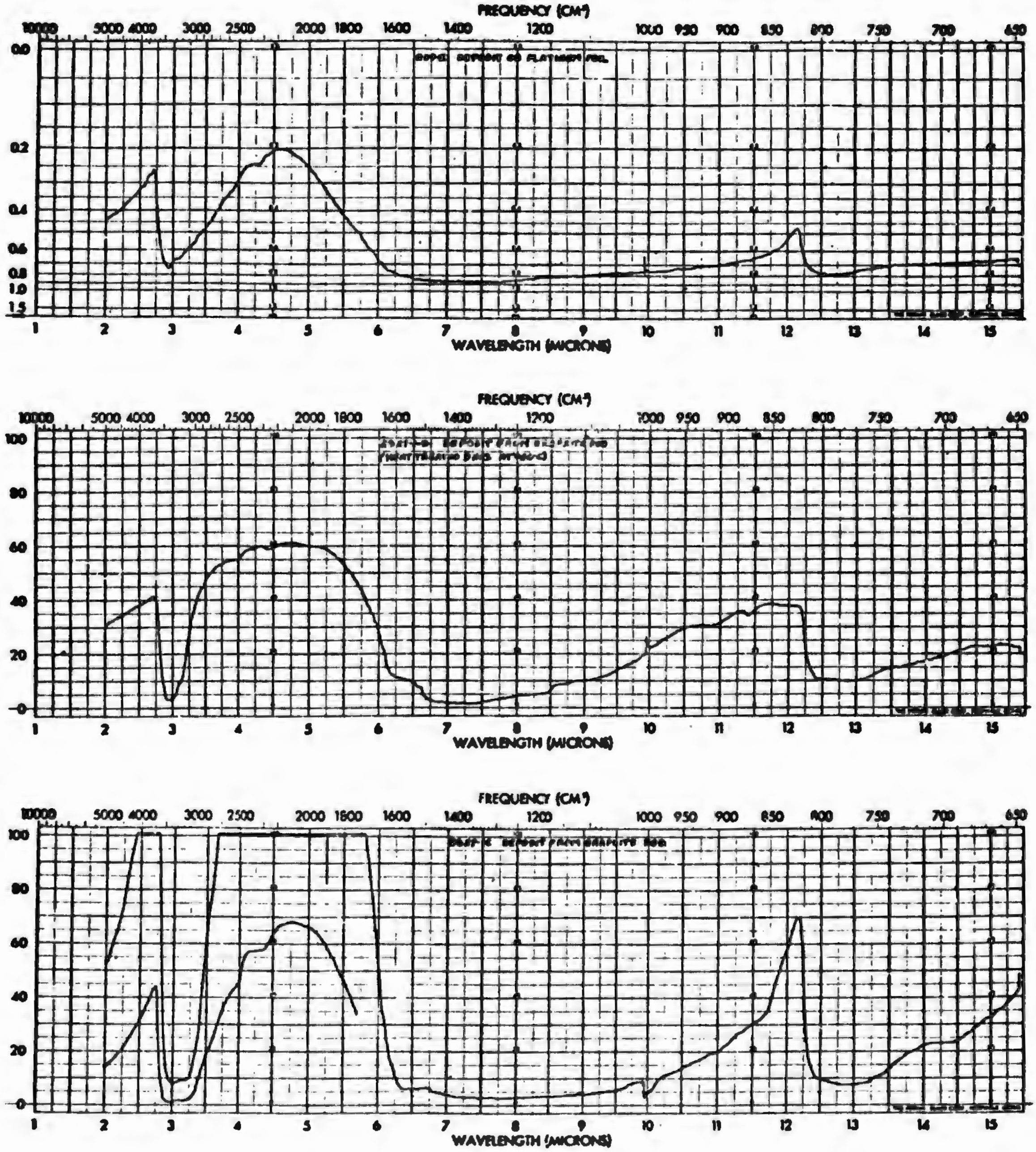


Figure 45. Infrared Spectra For Specimens R29-I, RB27-1D and RB27-1C.

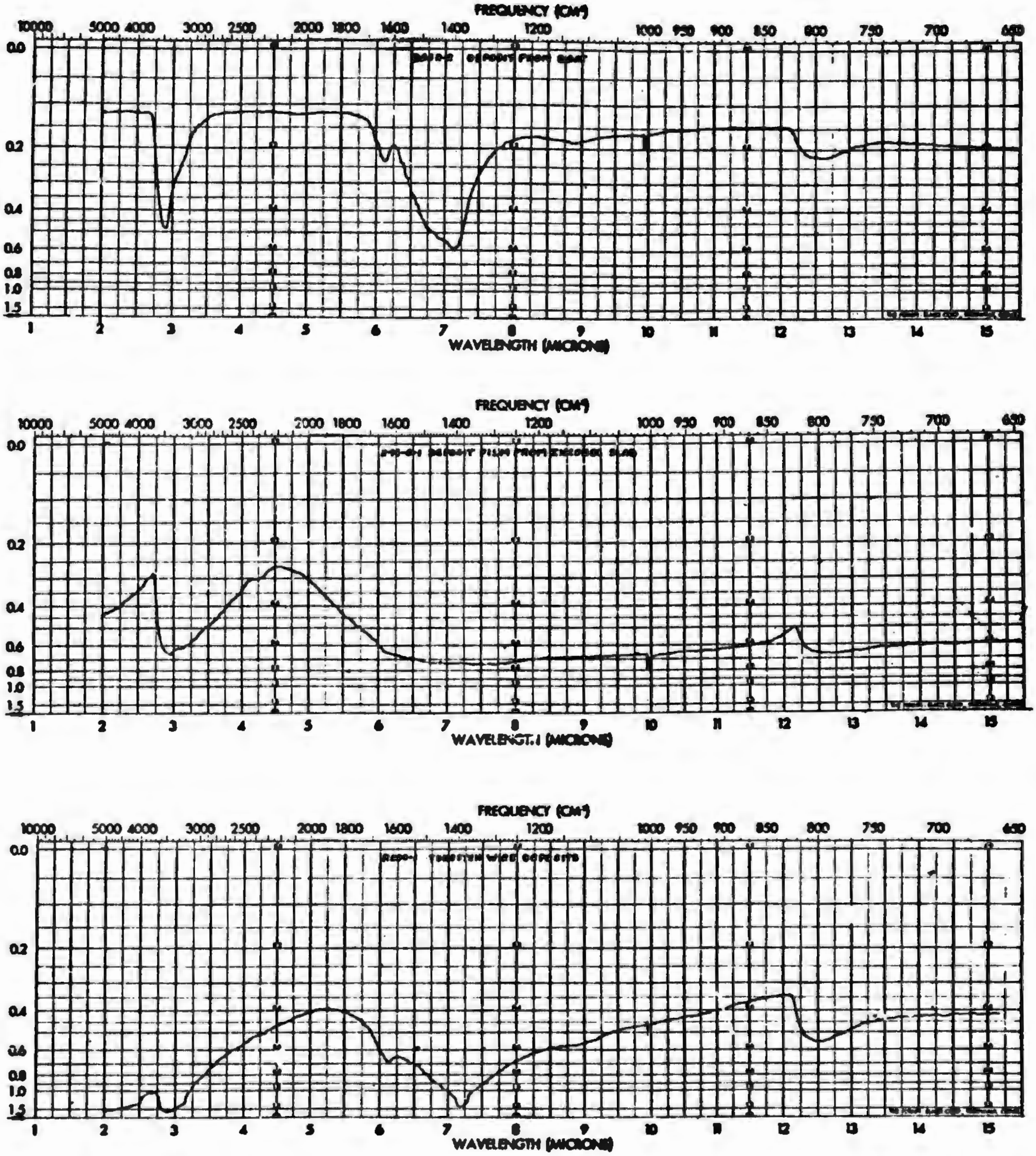


Figure 46. Infrared Spectra For Specimens R50Q-1, R53R-2 and R44-0-1

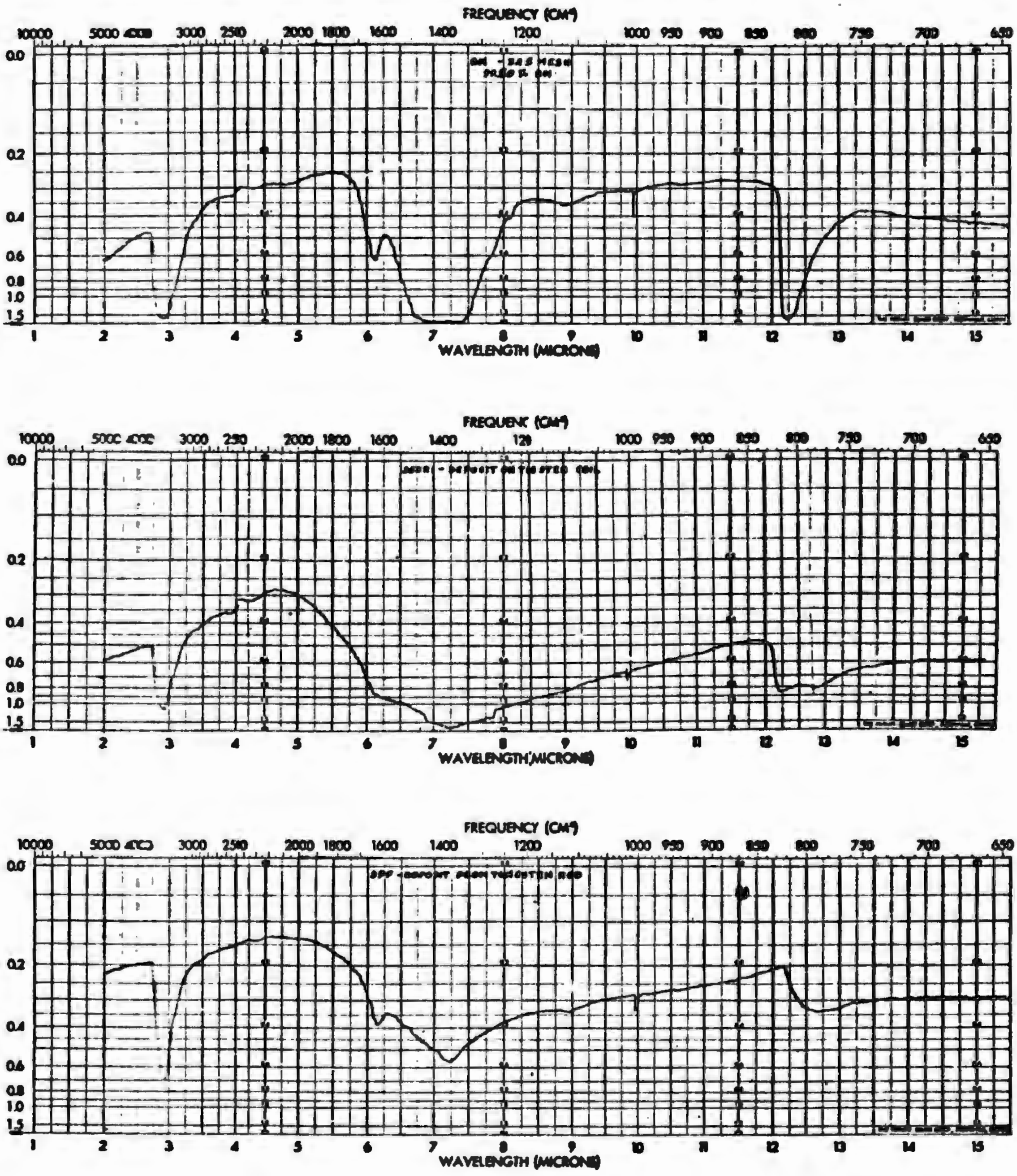


Figure 47. Infrared Spectra For Specimens S53-R1, S9F and 99.5% BN

while BN made at 800 C will begin to decompose after being exposed to air a short time, and that heated to about 1000 C showed only slight signs of decomposition after air exposure (12). Boron nitride heated at 1250 C is not attacked by boiling water (13). Since our films are formed by induction heating of the substrate, the films are formed at a lower temperature than that indicated at the surface of the substrate.

Chemical analysis has not been used because of the small amounts of the samples involved, the sample instability and analytical difficulties.

Since potassium vapor resistant and thermally stable BN coatings could not be produced in the substrates at or below the 1000 C maximum processing temperature, work in this approach was discontinued.

4.5.4 Vapor Deposition in Reduced Oxygen Environments

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 Al metal in about 10^{-3} mm. Hg pressure of O_2 leads to deposition of what are apparently suboxides of aluminum, and these oxidize to Al_2O_3 on exposure to air (14). Rate of deposition is about 1-5 A°/sec in coating thickness. Total thicknesses of 875A° are 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 Zr source at up to 1200-1400 C in an atmosphere of 10^{-3} torr of (flowing) O_2 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). Temperature was measured by optical pyrometer.

Similar deposition of Al_2O_3 from an Al source at about 800 C in an atmosphere of 10^{-3} torr of flowing O_2 did yield insulating deposits. These were very thin (unweighed) and apparently dense (microscopic investigation). The rate of deposition was lower than expected (15). Such films could be deposited on a substrate suitable for testing in K-vapor, but this was not done because of other troubles with them. It was found that in the atmosphere stated the Al source also became coated with oxide. As this oxide coating forms, thermal conduction from the heater -- which was either a tungsten wire loop or a tungsten wire coil heating an alumina crucible -- got poorer and evolution of Al slowed down. Under these conditions, oxide is deposited on the target, but slowly. Then the oxide coating on the source would break due to thermal motion of liquid Al and permit the metal to touch the heater, which had meanwhile risen to a higher temperature. The resulting puff of Al vapor would rapidly deplete the O_2 atmosphere, which led to deposition of conducting coatings on the target. Such conducting layers were probably composed of Al_2O_3 mixed with Al. No good way of avoiding this phenomenon was found. In view of these difficulties, the work on vapor deposition was terminated.

4.5.5 Formation of Alumina by Thermal Decomposition

Several unsuccessful attempts were made to vapor deposit alumina on spirals of tungsten and platinum wire by the same technique used with the BN. 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 because 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 no doubt was 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 was considered as a means of minimizing or eliminating the carbon problem. Another possibility was blowing the fairly volatile aluminum chloride over a hot substrate by moist argon might deposit Al_2O_3 on the substrate.

With the intention of eliminating the carbon formation problem experienced with aluminum isopropoxide, a quantity of aluminum methoxide was prepared. This compound has a much lower carbon content and does not contain the relatively easily cracked isopropyl group. A disadvantage found with the methoxide is its very low volatility. To pass aluminum methoxide vapors over a hot substrate, it will be necessary to incorporate into the deposition apparatus, a vacuum source capable of 10^{-5} torr.

Investigation of this technique was terminated to concentrate effort on the AlN formation investigation.

4.5.6 Formation of Aluminum Fluoride

A process for coating an aluminum substrate with AlF_3 by reaction with F_2 and/or HF has been developed by Bell Laboratories (9)(10). Such coatings are flexible and not limited in thickness by diffusion rates as in Al_2O_3 formed by direct Al oxidation. Coatings of 5 A° thickness have been made by Bell Labs. Such coatings can be oxidized to Al_2O_3, over the outer 1000th of their thickness by heating to 550 C in air. They might possibly also be converted to AlN by heating in NH_3. All of these reactions are non-shadowing and could be carried out on essentially finished wound coils. According to calculations, the AlF_3 itself would be thermodynamically unstable to K-vapor above about 550 C, but the Al_2O_3 of AlN might protect it.

AlN in the reasonably pure, dense state has a specific resistivity of about 10^6 ohm-cm at 850 C (16). 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 Al films on Inconel substrate with NF or F_2 at 500 C was set up. (This process was developed by Bell Labs. and is at present reported to be worked on by Allied Chemicals.) The action intended is:

$$Al^\circ + 6HF \rightleftharpoons AlF_3 + 3H_2$$

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 K-vapor. Therefore, it was intended that the AlF_3 formed will be partly or wholly converted to Al_2O_3 by direct oxidation. It was 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 K-vapor by the Al_2O_3. Work on this approach was terminated to pursue the more promising AlN formation approach.

4.5.7 Densification of Porous Coatings

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 experiment conditions allowing it to follow a thermal or other energy gradients. The principle is used in "hydrothermal" crystal growth of SiO_2. A possible solution has been found to the problem of accelerating material transport rates of refractory oxides to achieve dense structure without raising temperature above the limits of the wires to be used. Work done at Westinghouse Research by Dr. T. L. Chu indicates that reaction equilibria such as:

$$Al_2O_3\text{ (solid)} + 6HCl\text{ (gas)} \rightleftharpoons 2\,AlCl_3\text{ (gas)} + 3H_2O\text{ (gas)}$$

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 BeO with HCl 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 HCl pressure. Apparatus was set up in which a wire coated with finely divided refractory oxide will be placed in HCl gas at 10-15 atmospheres of pressure. The aggregate would be heated from the outside (periphery of the coated wire) and the end of the wire would be taken out to a cool zone so that a temperature gradient will exist across the granular insulation. What was expected in the system is 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_3 powder (Alcoa C1-6, 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 HCl and sealed. The charge was calculated to yield a pressure of about 10 atm. at 800 C. Half of the tube was stuck into a tube furnace and the other half with the target slides left outside. At 400 C and 700 C in the furnace reaction was very slow. At 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 deposit, in order. 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.

Analysis of the material transported toward the cooler side in the thermal gradient system involving the equilibrium

$$Al_2O_3 + oHCl \rightleftharpoons 2Al_2O_3 + 3H_2O$$

showed it to be Al_2O_3 in form of rather large crystallites. The crystalline portion comprised over 90% of the sample. The transported material contains 0.20% Fe whereas the source material only contains 0.03% Fe. The transported material also contains a residual 1.2% of Cl.

The Al_2O_3 used as source material had changed color to dark grey after the transparent experiment. This color was traced to contamination with carbon of unknown source. Our conclusions are: (1) transport of Al_2O_3 to a desired location does take place at a useful rate, (2) the transported Al_2O_3 is deposited largely in the crystalline form (which is probably necessary, for resistance to K-vapor), (3) iron present as an undesirable impurity is transported even more rapidly than Al_2O_3 and probably by a similar mechanism, (4) the Cl found can be removed by after bake of the sample, (5) an unknown, probably organic, contaminant is present in the system and acts as a source of carbon.

The apparatus was set up to try transport of Al_2O_3 on a wire mock up. The simulated wire was tantalum to prevent any attack by the HCl environment. A porous Al_2O_3 coating was applied to the Ta rod from a slurry. The baked out coating on simulated Ta wire popped off on cooling due to oxidation of the Ta in the furnace. The N_2 and A_2 cover gases were apparently contaminated. Reruns produced adherent, porous Al_2O_3 coatings.

Investigation of this technique was terminated to concentrate effort on more promising solutions and more pressing problems such as the metal-ceramic seal for potassium vapor applications.

4.5.8 Formation of Aluminum Nitride

It has been reported by The Renner (18) that films of aluminum nitride can be deposited on a graphite disc by passing vapors of the $AlCl_3 \cdot NH_3$ addition compound over the disc heated to 1000-1700 C. Films deposited at the higher temperatures have better formed crystal structures, are whiter, and are more chemically stable than those found at lower temperatures. Renner states that white AlN is hardly attacked by hot water, dilute or concentrated HCl, HNO_3, H_2SO_4 or aqua regia. It is decomposed by hot concentrated NaOH as represented by the equation:

$$AlN + OH^- + 3H_2O \rightleftharpoons Al(OH)_4^- + NH_3$$

This addition compound was prepared by passing anhydrous ammonia over $AlCl_3$ at about 150 C until the gross composition of the reaction mixture was $AlCl_3 - 3NH_3$. This is a mixture of compounds containing various ratios of aluminum chloride to ammonia. It was then heated to 350 C for several hours. In this treatment, excess ammonia is driven off giving a composition corresponding to $AlCl_3 \cdot NH_3$. This was purified by distillation at 170 C/0.02 torr. The product is snow white solid with a melting point of about 125 C. It is sensitive to moisture but is quite thermally stable up to its normal boiling point of 420 C.

The apparatus consisted of a straight 30 mm diameter quartz tube in which was placed one porcelain boat containing $AlCl_3 \cdot NH_3$ and another, about 6 inches farther downstream, containing the substrate. A resistance heater was used to heat the portion of the tube containing the source material while the substrate was heated with a radio frequency coil which surrounded the tube at the location of the substrate. All depositions were carried out in a continuously pumped system at a pressure of about 10^{-2} torr. Time of a typical run was about 4 hrs.

Vapors of the source material were passed over graphite rods heated at 1000 to 1550 C. The temperature of the source material was varied from 125 to 200 C corresponding to vapor pressure of about 10^{-2} to 10^{-1} torr. At this higher temperature, the material showed little tendency to deposit on the graphite, but at 1000 C, well bonded continuous insulating films were obtained. Unsupported films of the coating were obtained by heating for several hours at 700 C a coated graphite rod which had been cut in half. The rod was partially burned away so that it was easily separated from the film. Portions of this film were soaked in water and dilute HCl for several weeks with no apparent deterioration. A very small amount of gelatinous precipitate formed in a sodium hydroxide solution in which a piece of the film was soaked for 3 weeks. Elemental analyses are being determined on the film.

An X-ray diffraction pattern was obtained on a portion of the coating which chipped from an unusually heavily coated end of a graphite rod. The rod and separated disc are shown in Figure 48. The diffraction pattern corresponds to a hexagonal wurtizite crystal structure which aluminum nitride is known to have.

An aluminum nitride coated graphite rod and a piece of unsupported AlN film have been submitted for potassium vapor exposure tests. The unsupported film of AlN, sample CK-27, was unaffected by the 172 hour exposure to K-vapor at 850 C, however, the AlN coated graphite, sample CK-28, disintegrated during some period of exposure. The AlN coating on the graphite was evidently not a continuous, pin hole free one.

A 20 mil molybdenum wire coil was heated to 935 C in the presence of $AlCl_3 \cdot NH_3$ vapor. A thin adherent insulating film was found on it. A 20 mil tungsten wire coil was heated to 970 C in the presence of $AlCl_3 \cdot NH_3$ vapor. The coating was about 1 mil thick. Several attempts were made to apply aluminum nitride to coils of Oxalloy 28 but all were unsuccessful. Any coating which was formed chipped off as the wire cooled. A photograph of one such coil is shown in Figure 49. During runs with Oxalloy as the substrate, a cloudy yellow film formed on the quartz tube. This might indicate that the source material is reacting with the wire giving a surface to which the AlN will not adhere. To determine whether a metallic chloride was being formed on the wire surface as a result of reaction with $AlCl_3 \cdot NH_3$, an Oxalloy coil, which had been exposed to the addition compound at 900 C, was put into water. However, a test for chloride ion in water was negative. While the coil was in water, a loose rusty sediment formed on it. This did not occur in a similar coil which had not been exposed to $AlCl_3 \cdot NH_3$ at 900 C.

An Oxalloy 28 wire coil which had been plasma sprayed with about 25 mils of alumina was exposed to $AlCl_3 \cdot NH_3$ vapors at 875 C. Two anticipated troubles with this experiment did not materialize. It was feared that the difference in the thermal expansion of the wire and alumina would cause spalling of alumina at 875 C. This did not occur. Another anticipated problem was that the interface between the alumina coating and the wire would make it difficult to bring the

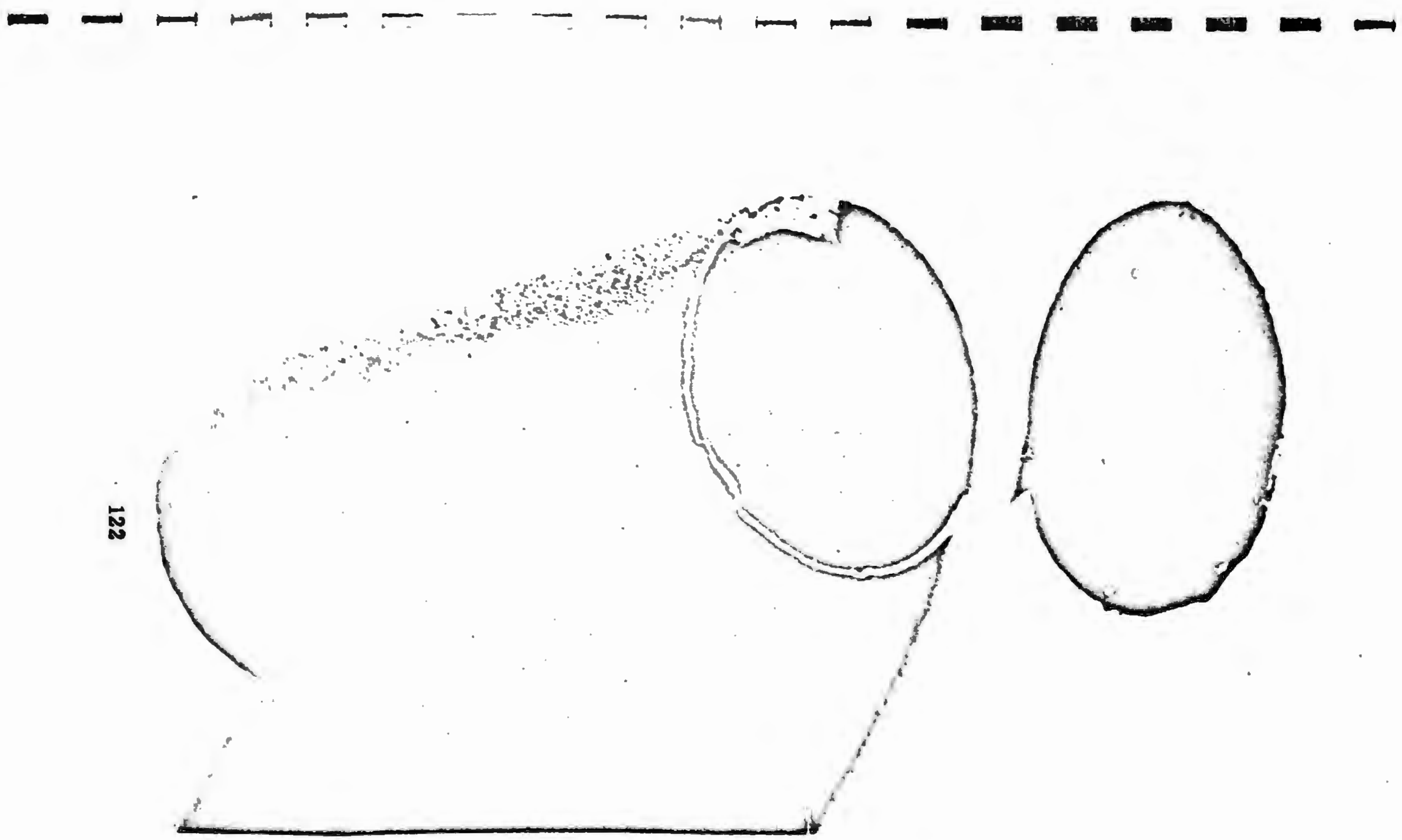


Figure 48. Heavy Pyrolytic Aluminum Nitride Coating Chipped From Graphite Rod

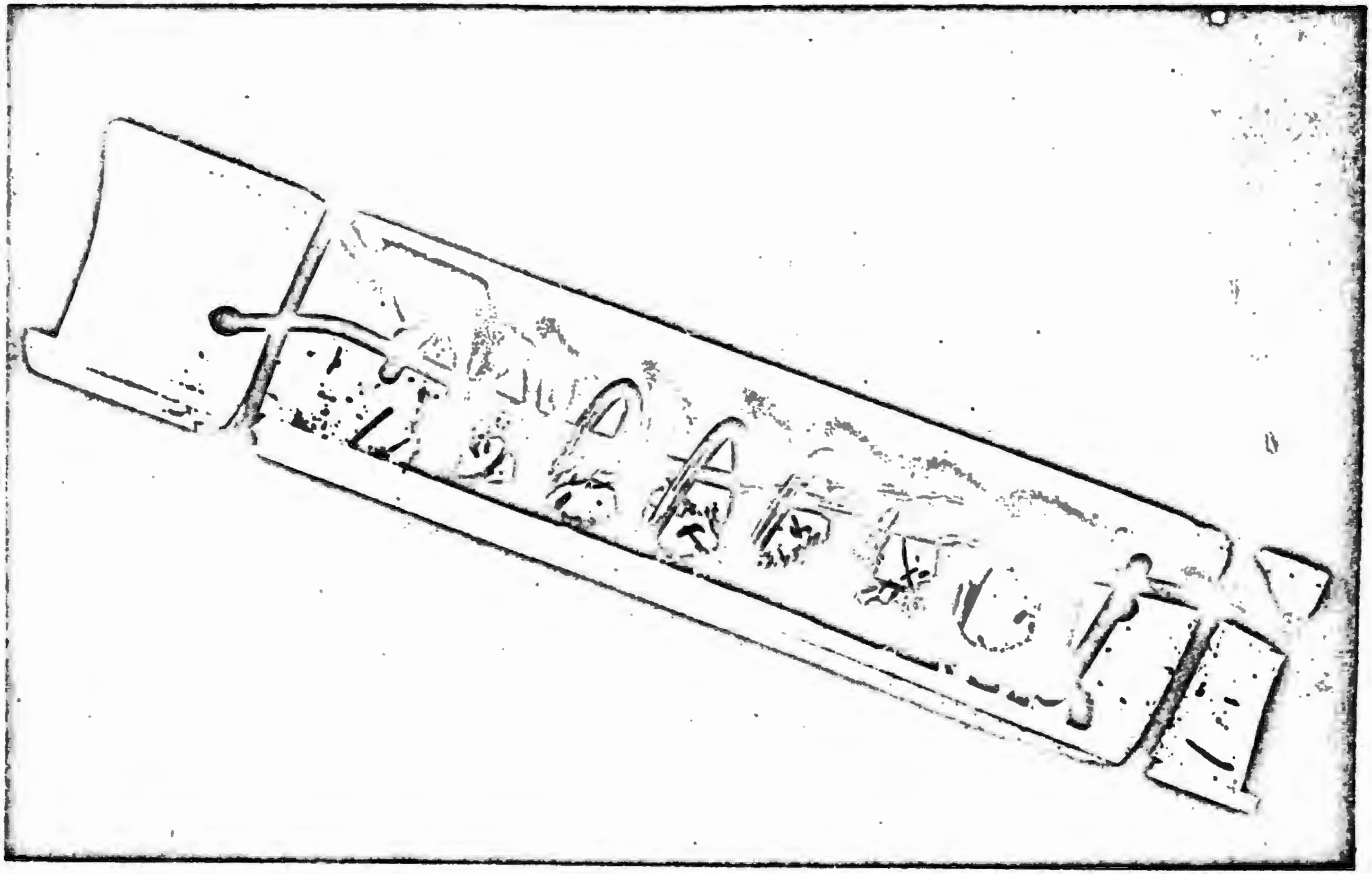


Figure 49. Pyrolytic Aluminum Nitride on Oxalloy 28 Wire

alumina up to the temperature. However, no difficulty was encountered in heating the alumina surface to 875 C. Apparently it is well bonded to the wire.

As the vapors of $AlCl_3 \cdot NH_3$ were brought into contact with this alumina coating, areas of a green film formed on the alumina. These were somewhat conductive. They seemed to originate at cracks in the alumina coating. Figure 50 is a photograph of this coil. Another coil with a thinner alumina coating, without apparent cracks, was also exposed to $AlCl_3 \cdot NH_3$ vapor at 875 C. A fairly uniform dark grey coating covered the alumina. It was not conductive. Figure 51 shows this coil alone with another alumina coated coil which was not exposed to $AlCl_3 \cdot NH_3$ vapor.

The Oxalloy 28 wire coil which had been plasma sprayed with alumina and then overcoated with vapor deposited aluminum nitride (sample CK9) was exposed to potassium vapor at 850 C for 170 hours. During this treatment much of the alumina chipped off, leaving unanswered the question of how much protection is offered by the AlN. A disk 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. It suffered no ill effects.

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 ($AlCl_3 \cdot NH_3$) 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.

In view of the fact that thin films of AlN 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 AlN, might be the controlling factor in the successful vapor deposition of

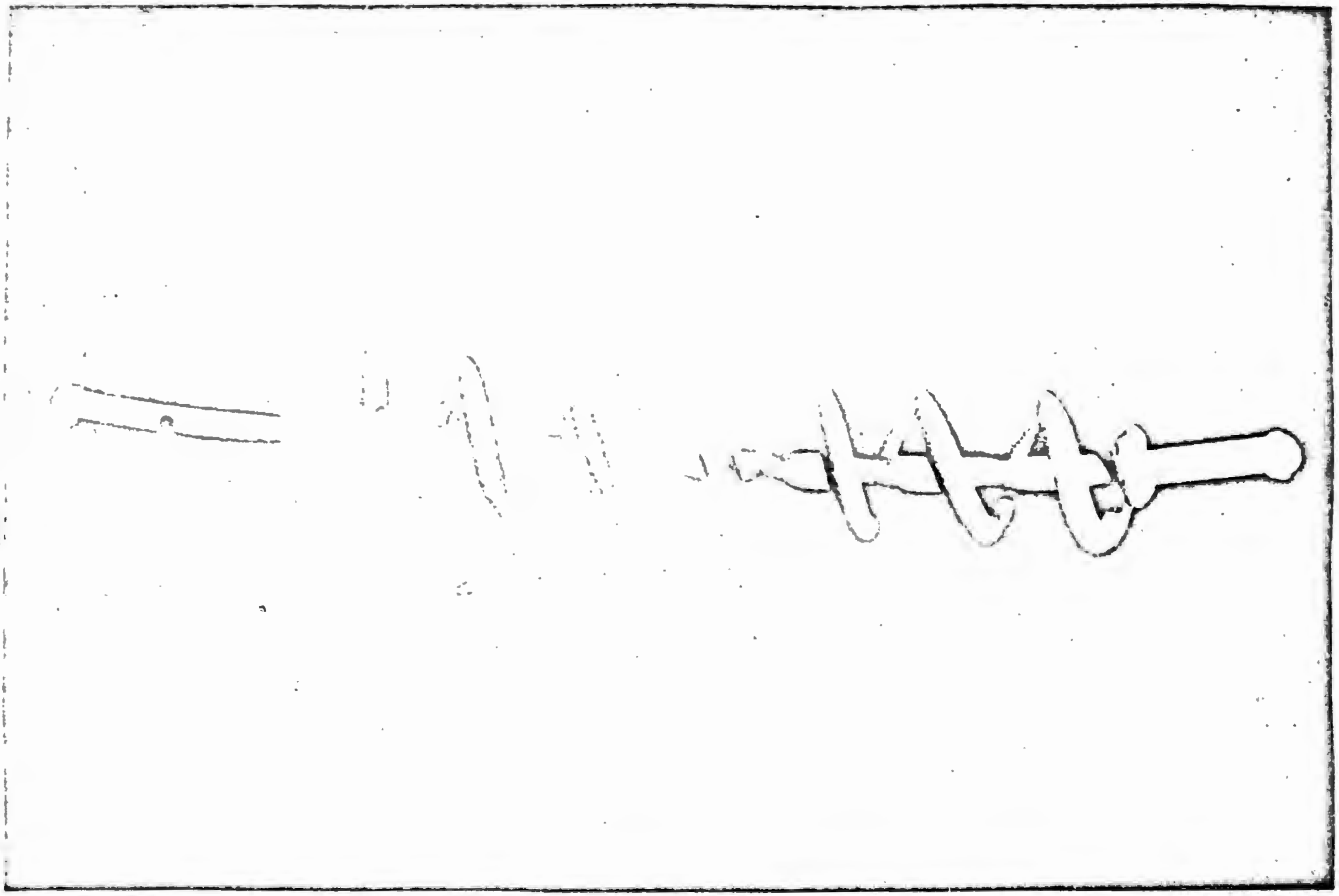
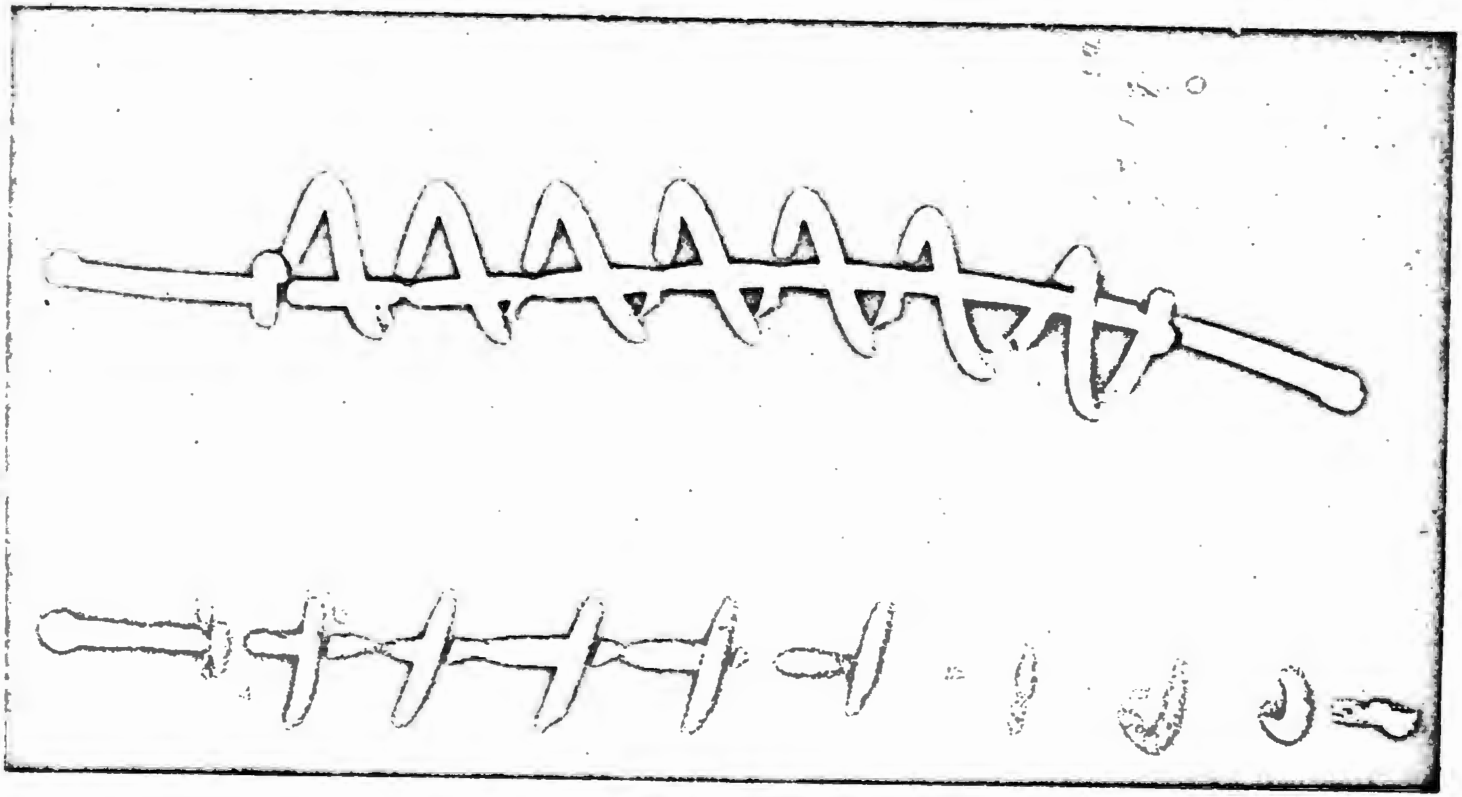


Figure 50. Plasma Sprayed Alumina Coating on Oxalloy 28 Wire After Exposure to $AlCl_3 . NH_3$. Wire Temperature During Exposure Was 875°C.



Top - Plasma sprayed alumina coated Oxalloy 28 wire.
Bottom - Similar alumina coated coil with pyrolytic aluminum nitride film.

Figure 51. Coated Oxalloy 28 Coils

aluminum nitride under our 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. The sample was submitted for resistivity measurements at 850 C in argon. In addition, similar resistivity measurements were made on AlN coated Mo rod and on an unexposed version of the AlN overcoated zirconia coated Ni clad Ag.

4.5.9 Plasma Spray Applied Coatings

All plasma spray coating of substrates was done using a Metco Model 1B Plasma Spray Unit equipped with a standard nozzle for ceramics. The carrier gas used was argon and initial spray trials were made using internal nozzle injection of powders. Various oxides were plasma sprayed onto several substrates to optimize processing parameters and obtain samples for adherence tests and metal vapor exposure tests. A list of the materials plasma sprayed and substrates on which they were sprayed are given in Table 13.

Satisfactory coatings were obtained with all materials used. The substrate, when properly prepared by solvent cleaning and light sandblasting was easily coated in all cases.

Samples of each oxide on an Inconel substrate were subjected to thermal cycling to 850 C. The samples were heated from room temperature to 850 C over a period of 1-1/2 hours and allowed to cool in still air to room temperature. No evidence of separation of the coating from the substrate was found on any of the samples.

TABLE 13
PLASMA SPRAYED MATERIALS AND SUBSTRATES USED

Oxides	Substrates
Modified Alumina (Metco 101)	Inconel Strip Nickel Rod
Pure Alumina (Metco 105)	Inconel Strip Inconel Clad Copper Stainless Steel Clad Copper Nickel Bar
Zirconia, Hafnium Free Lime Stabilized (Metco XP-1115)	Inconel Strip Nickel Bar
Zirconia (Metco 201)	Inconel Strip
Magnesia (Norton)	Inconel Strip Nickel Bar
Non-oxides	
Nickel-Aluminide (Metco 404)	Inconel Strip Nickel Bar

A system was devised and built for holding preformed coils of wire in a fixture which could be continuously rotated during the plasma spraying operation. Using this equipment, a preformed coil of nickel clad copper was plasma coated with alumina (Metco 105). The above coil was used for initial coating tests because it was available from another project and was very similar to the statorette coils. A photograph of the coated coil is shown in Figure 52. The coating generally was very uniform and adherent. One small area which had excessive build up of the oxide cracked when the coil was compressed. This crack appeared at the apex of the acute angle on the end of the hexagonal coil. Additional coils preformed to the exact size to be used on the statorettes were constructed using AWG No. 8 nickel clad silver wire. These coils were coated with alumina (Metco 105) and again had a very uniform thin coating. When these coils were compressed, no visible cracking or loss of coating occurred. Better adherence is expected on these latter coils since the ends of the coil have a uniform radius and therefore do not concentrate the bending stresses at the ends as do the initial evaluated hexagonally shaped coils.

The plasma coated oxides on Inconel substrate were subjected to potassium environment tests. The results of these tests are given in Table 1, (Sec. 4.1). The alumina Metco 101, was attacked probably through the titania additive in the material. The pure alumina Metco 105, seemed to be intact and unaffected but separated from the Inconel substrate. The hafnium-free zirconia, Metco XP-115, was virtually unaffected and no change in appearance occurred. The calcia stabilized zirconia, Metco 201, remained as an insulating film after exposure but appeared from weight loss and color change to have lost the calcia.

The sample of zirconia sprayed onto an Inconel substrate looked sufficiently good after exposure to K-vapor at 850 C that a coil was prepared with this coating. 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.

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

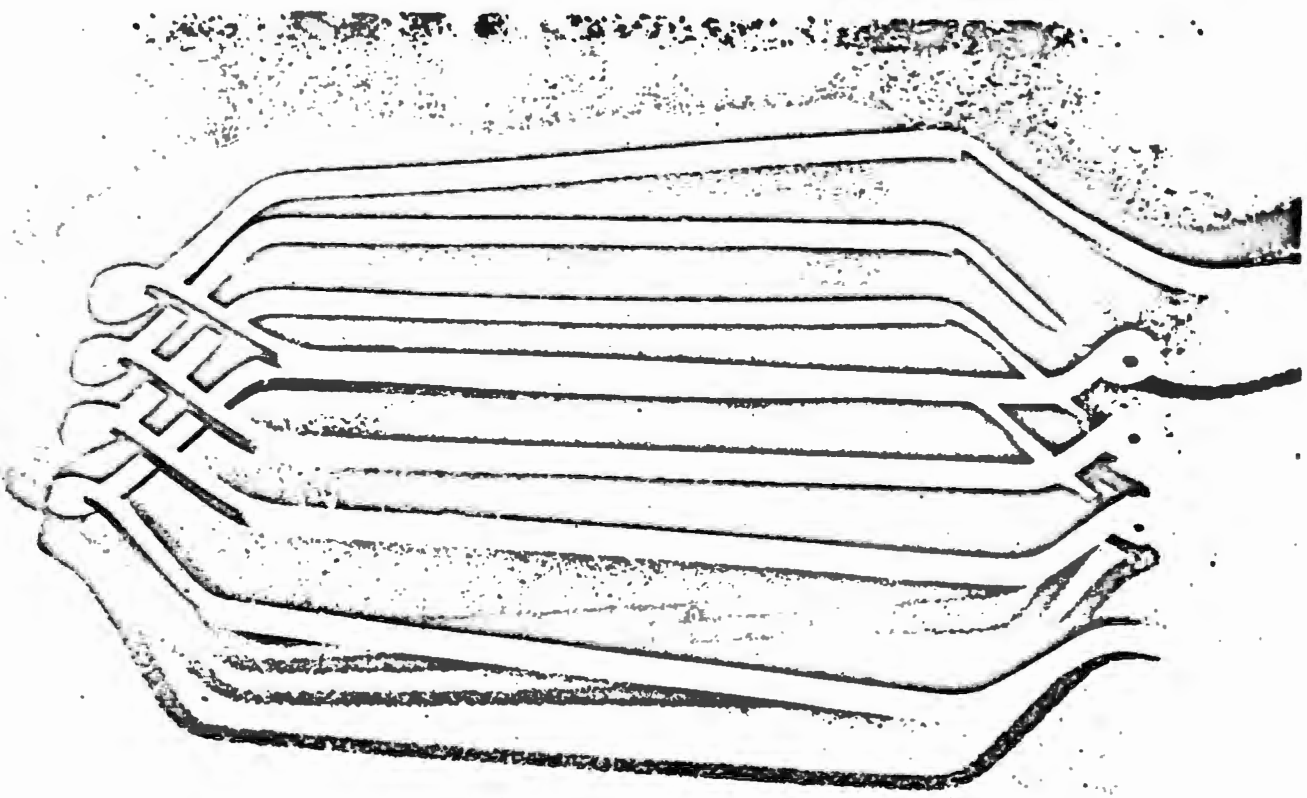


Figure 52. Preformed Nickel Clad Copper Coil Plasma Coated with Alumina

of one end. These were submitted for potassium test to determine the adherence and resistance to potassium of these insulations when on actual conductor materials.

The adherence of plasma sprayed coatings to nickel clad silver wire is not as good as to Inconel strip. Both substrates were sandblasted 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.

The failure of the coated wire samples in potassium, as indicated in Table 1 (Sec. 4.1), was attributed to adherence failure. The coatings which lifted were examined under a microscope and no attack on the coatings 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.

A new source of plasma spraying grade of strontium zirconate was located and a trial lot of the material obtained. Direct spraying of the strontium zirconate onto 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.

In order to interpret the results of the potassium environmental tests on various insulators, it was necessary to know the impurity content of the materials used. Table 14 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.

4.5.9.1 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

TABLE 14
PURITY OF VARIOUS INSULATORS TESTED FOR POTASSIUM RESISTANCE

Material	Al_2O_3	MgO	ThO_2	ZrO_2	CaO	BeO	SiO_2	TiO_2	Fe_2O_3	Ma_2O	SrO	BaO	BN	Unknown
Alumina AD99	99.0													1.0
Metco 101	91+						3*	2.3*	2*					1.0*
Metco 105	96+						2*			1*				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					
Metco 201	0.5			93.5	5.0		0.35							0.65
Thoria			99.5+											0.5*
Beryllia						99.5								0.5
Magnesia														
Single Crystal	.02	99.5+			0.01		0.08		0.05					
Flame Spray	0.26	96.4			1.91		1.21		.23					
Strontium Zirconate														
Y-628	0.07	0.24		53.9			0.24	0.07			45.3			
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		40.6	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					

+ Minimum * Maximum

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%).

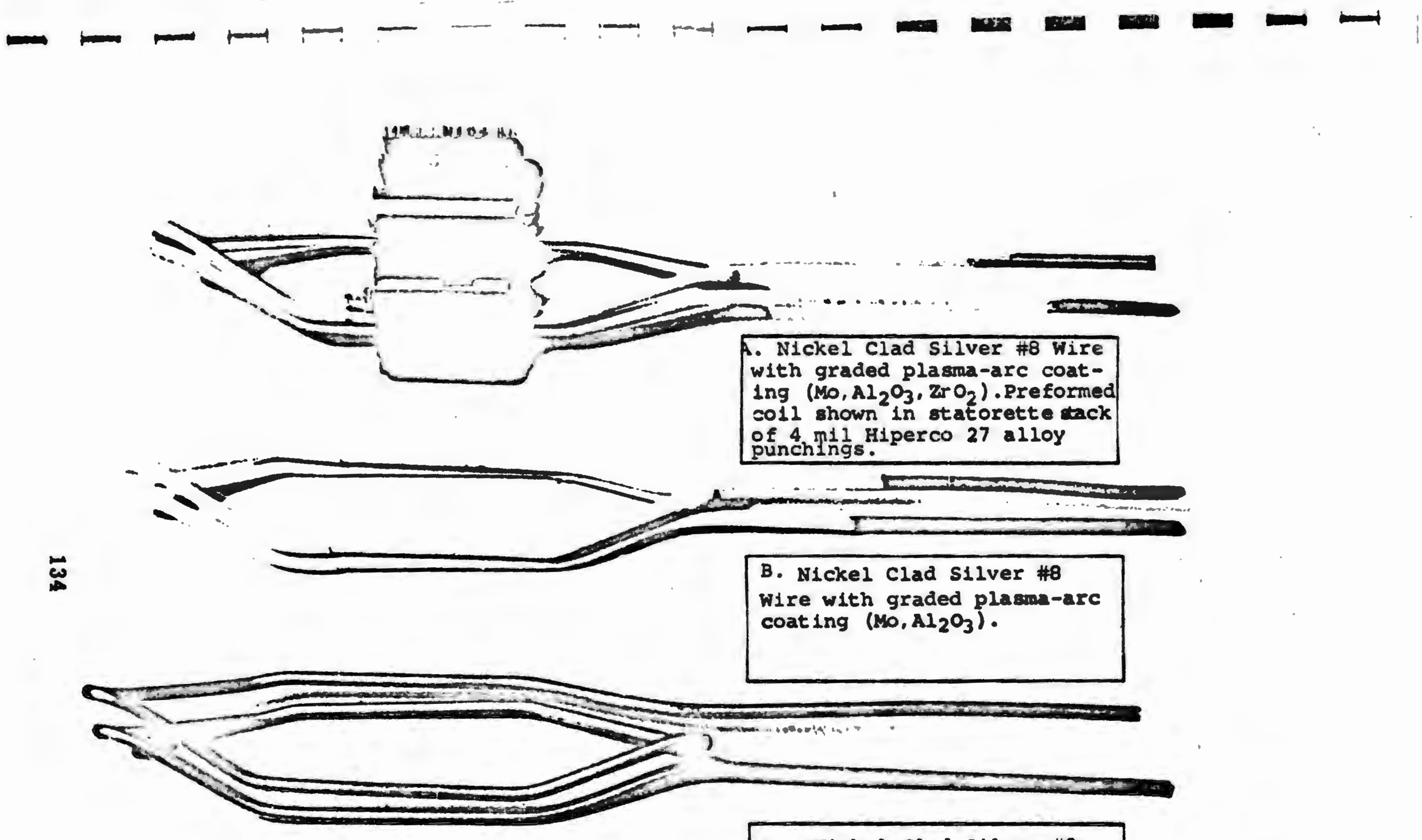
4. A two mil coating of molybdenum, two mil coating of zirconia, followed by a two mil coating of alumina (99%).

Figure 53 shows examples of coated and uncoated nickel clad silver conductors.

4.6 Discussion of Coating Methods

In consideration of the technical problems in coating conductors and the results of the potassium environment tests, the choice of usable conductor insulations is very limited. The plasma sprayed zirconia appears to be the best coating as far as resistance to potassium vapor, but does not have as high an insulation resistance at high temperatures as the other insulating materials. The use of an AlN overcoat on the zirconia appears to raise the resistivity value to an acceptable level (1.8 x $10^4 \Omega$) at 850 C. Electrical data on the insulation system after exposure to potassium vapor at 850 C for 172 hours was not obtained because the loss of the silver core during exposure formed a somewhat conductive layer on the coated wire.

The favorable values (4.0 x $10^5 \Omega$ at 850 C) of the thin AlN coating on the Mo rod indicate that precoating the Ni or Inconel clad silver conductor with Mo and using only AlN as the insulation, has promise.



A. Nickel Clad Silver #8 Wire with graded plasma-arc coating (Mo, Al_2O_3, ZrO_2). 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, Al_2O_3).

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

Figure 53. Preformed Nickel Clad Silver Coils With and Without Ceramic Insulation

Plasma sprayed alumina is another candidate and may prove successful on round conductors. The alumina would be a better electrical insulator but adherence to the metal substrate during exposure to potassium vapor has been a problem. The fusion coating of alumina and zirconia has failed to pass the potassium vapor test even though the basic materials are resistant to K-vapor.

The work on AlN coating formation did not progress to the point where AlN could be applied uniformly to the size and configuration of coil needed for the statorette tests. Largest coils successfully coated were 3/4" diameter spiral coils about 1-1/2" long. The statorette coils would require modification of the test apparatus substrate heating system and possibly modification of the deposition technique. Based on the experience gained to date, it is felt that use of a Mo undercoat with high purity plasma spray applied strontium zirconate or alumina would provide a potassium vapor resistant insulation good for 850 C. An overlayer of zirconia could be used to provide an additional barrier layer to the potassium vapor.

The BN coating also offers promise where a conductor could be used that can withstand a temperature of 1450 to 1500 C.

4.7 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. I 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 54 shows the statorette test assembly. The following test conditions were imposed on this assembly.

4.7.1 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

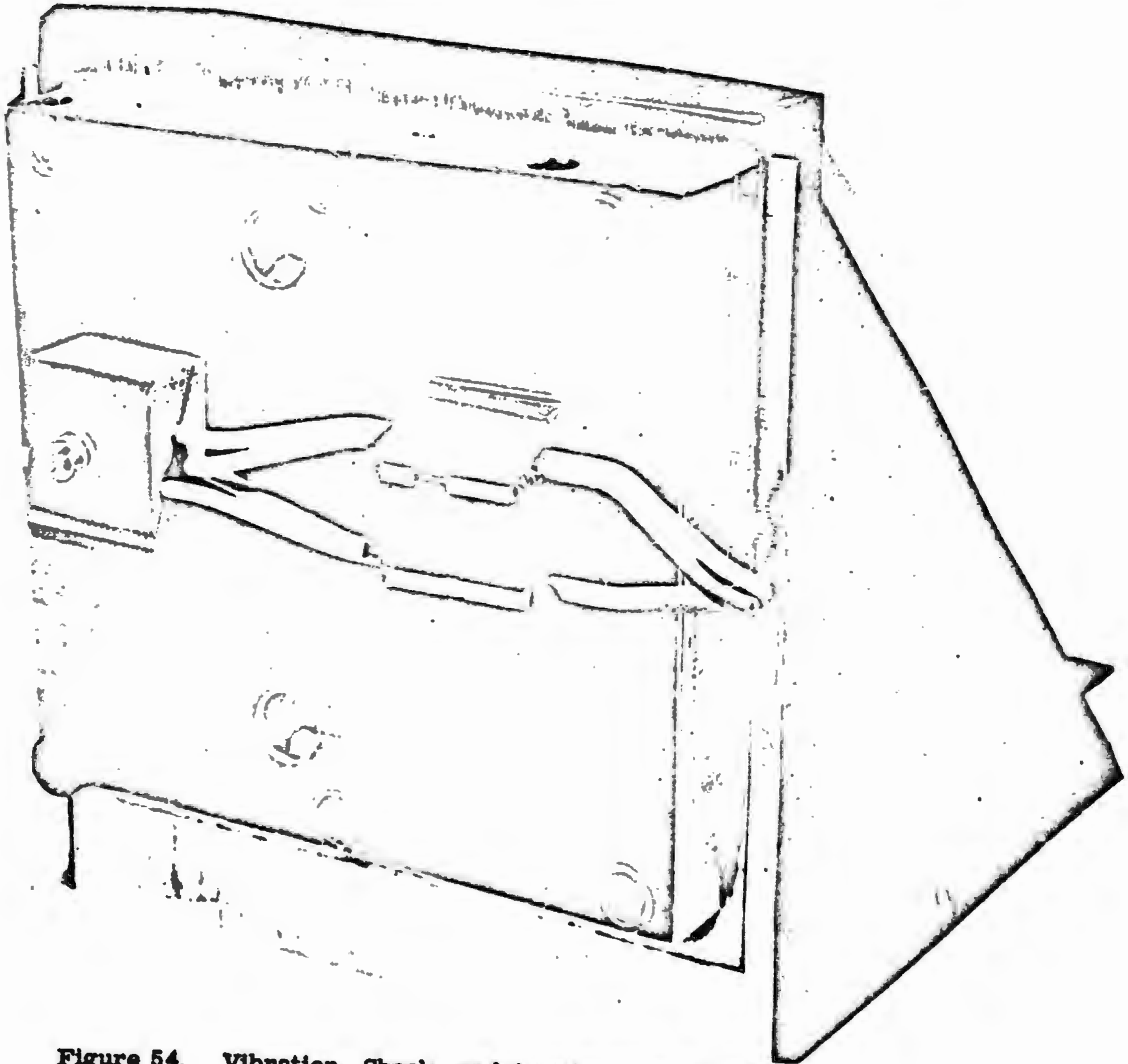


Figure 54. Vibration, Shock, and Acceleration Test Fixture - Sample 1 and 2 After Adherence Tests

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 ~ 23 C.

4.7.2 Shock

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

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

4.8 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.

4.9 Potting Compounds

Potting compounds in this program 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 to 850 C because of their good insulation resistance. These are the first five materials listed in Table 15. Since there is some indication that the binders for these compounds might be affected by potassium vapor, other

TABLE 15
PROPERTIES OF POTTING COMPOUNDS

Sample	Filler	Binder	Green Strn.	Strn. after Exposure		Shrinkage	
				To 550 C	To 875 C	Green	Fired
Saureisen #9	Powder	Water	Fair	Poor	Poor	Low	ca 1%
Sauereisen #30	Powder	Water	Fair	Fair	Fair	Low	ca 3%
Sauereisen DW 30	Powder	Water	Fair	Good	Fair	Low	ca 2.5
VG 107	Silicates	Phosphate	Good	Excellent	Very Good	ca 2%	ca 3%
W839	Silicates	Phosphate	Good	Very good	Excellent	Low	Low
S 7-63-1	Alumina	Colloidal Zirconia	Poor	Fair	Good	High	---
S-7-63-2	Alumina	Mag. Metholate	Very Poor	None	None	High	---
*S-7-63-3	Magnesia	Colloidal Zirconia	Fair	Fair	Fair	High	---
S-7-63-3	Magnesia	Mag. Metholate	Poor	None	None	High	---

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

compounds (6 through 9) were formulated using collodial oxides as binders. Samples have been prepared for tests in the two vapor environments.

The samples of potting compound exposed to the potassium vapor are listed in Table 1 (Section 4.1) as PK-1 through PK-5. The sample PK-1 was zirconia bonded magnesia. PK-2 and PK-4 were Sauereisen cements No. 30 and 9 respectively. The PK-3 and PK-5 potting compounds were Westinghouse compositions using phosphate bonds. The last four materials had been tested prior to this program and were, in our opinion, the best available for evaluation in potassium. However, it was believed that most bonding materials for potting compounds would be attacked to some degree. The compound PK-1 was developed and used because it contained only known potassium resistant materials. (At least in their desne fused state.) All samples failed by disintegration, probably from attack of potassium on the bonding material.

4.10 Radiation Tests

Two insulated conductor coils were sent to Brookhaven National Laboratories for exposure to a nuclear pile radiation environment. The total dosage given these insulated conductors was 1.8×10^{19} thermal neutrons and 5×10^{8} rads gamma. The results of this radiation exposure are given in Table 16. A comparison of the electrical resistance before and after irradiation shows a decrease in electrical resistance in both insulation coatings.

4.11 Potassium Vapor Exposure - Life Tests

An Alite cable end seal was obtained that had been fabricated from materials previously shown to be resistant to K vapor at 850 C. The weak spot in this seal was the copper braze between the "A" nickel metal piece and the metallized ceramic. This was protected by an over spray of nickel aluminide. The seal was then welded into a half inch Swagelok adapter. Potassium was loaded in this electrical test capsule. Electrical resistance measurements were conducted on this capsule terminal seal at various temperatures to 850 C. The results of this experiment are shown in Figure 56.

A statorette test capsule for potassium vapor exposure of a nickel clad silver coil was fabricated from three inch stainless steel pipe, type 316.

Alite terminal seals, prepared as previously described for protection against the corrosion by potassium vapor at 850 C, were used for electrical terminals in this test capsule. A coil of nickel clad silver conductor No. 8 AWG was inserted in a Hiperco statorette. This conductor was previously coated with nickel aluminide, zirconia and alumina. The silver exposed at the ends of

TABLE 16
ELECTRICAL RESISTIVITY OF INSULATED CONDUCTORS BEFORE AND AFTER NUCLEAR EXPOSURE

	Radiation Total Dose			Resistance	
	Neutrons	Gamma	Insulation	Ohms After	
Insulated Conductor	Thermal	Rads	Before Exposure	Exposure	Comments
Inconel Clad Silver Molybdenum Undercoat Al_2O_3 over Zr O2	1.8×10^{19}	5×10^{8}	2.9×10^{10}	1.3×10^{8}	50% Physical damage - Coating came off wire
Inconel Clad Silver Nickel Aluminide Undercoat Strontium Zirconate	1.8×10^{19}	5×10^{8}	2.0×10^{11}	3.0×10^{6}	No evidence of physical damage

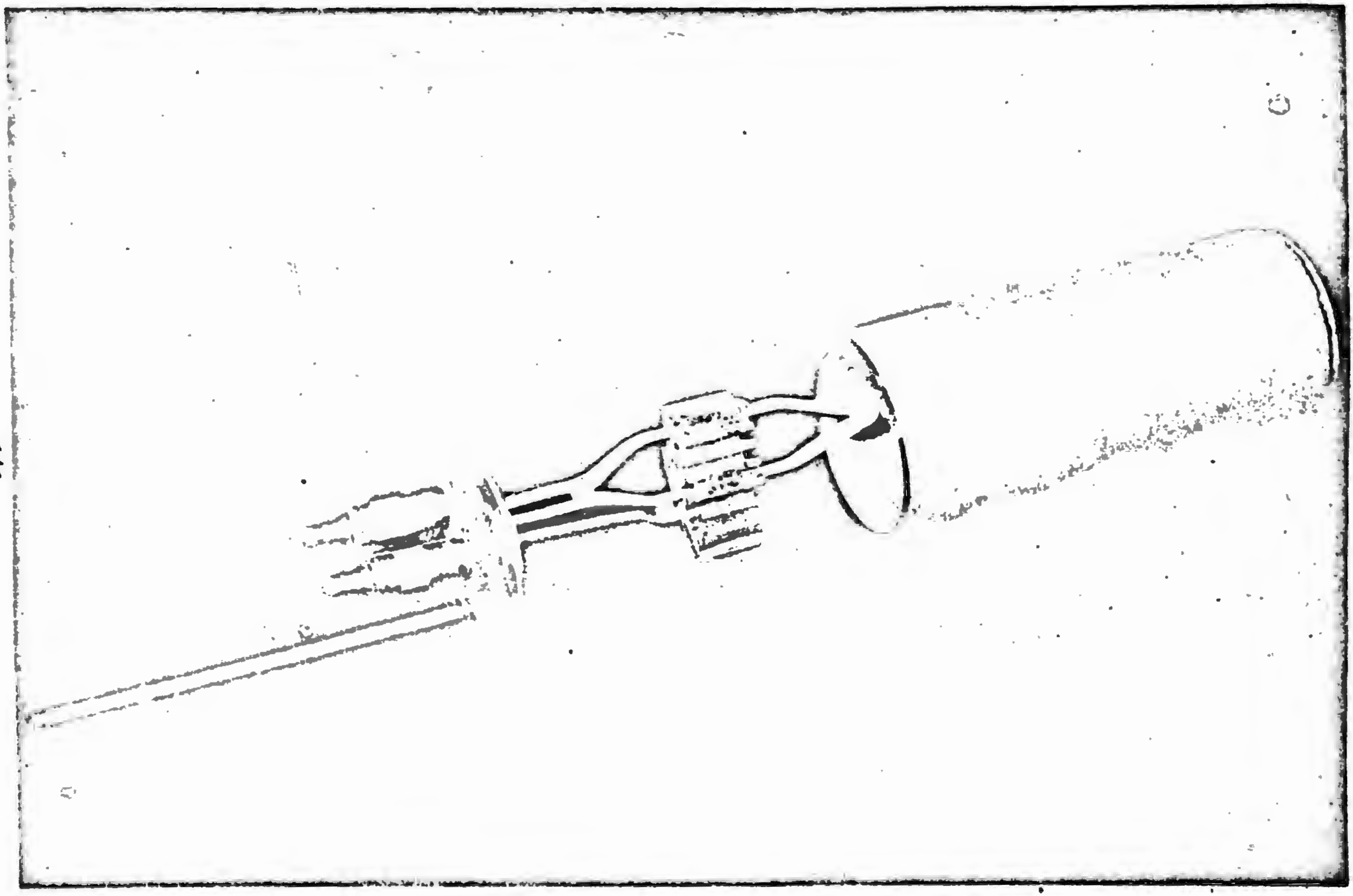


Figure 55. Exploded View of Statorette Potassium Vapor Test Capsule

this conductor was protected from the corrosive action of 850 C potassium vapor by first nickel plating, then shrinking a stainless steel rod with a hollow end over the conductor ends. The joint was then over-sprayed with nickel aluminide followed by zirconia-alumina insulation. This assembly is shown in Figure 55.

Twenty grams of MSA purified potassium containing $<$ 50PPM of oxygen was introduced into this test capsule via a fill tube. The sealing and filling operation was conducted in a vacuum dry box at 10^{-3} torr. After charging the capsule with potassium, it was placed inside an argon-vacuum furnace for life testing of the conductor.

The furnace was evacuated then flushed with purified argon. The test atmosphere in the furnace was argon at ~ 4 inches of water pressure.

Electrical leads were attached to the terminal end seals and capsule so electrical measurements could be conducted at temperature (850 C).

The electrical resistance measurements at temperature were on the order of 1×10^4 ohms, however, the furnace failed after eight hours terminating this exposure. The furnace was repaired and testing resumed for approximately 172 hours. The results of the experiment are inconclusive, as the potassium had attacked the seals severely and reacted with the furnace lining at some time during this exposure.

The test capsule was cut open after first neutralizing the potassium with methanol for safety considerations. Figure 57 shows the effect of the oxidized potassium vapor on the coil.

The joints that had been oversprayed with nickel aluminide and alumina were not severely attacked. The insulation around these joints was intact and had a breakdown voltage of 500 volts with an a. c. leakage of 40 micro amperes at 500 volts.

The coating around the surface of the clad conductor was attacked at the interface of the nickel cladding. This attack may be visually observed in Figure 57.

Although the terminal end seals were still intact, inspection of the metallized surface showed attack at the interface of the molybdenum-manganese metallizing and OFHC copper brazing. The nickel aluminide protective coating that was plasma-arc sprayed over the copper braze was not attacked. The potassium apparently had gone through pinholes in this protective coating and removed the copper braze causing the seal to leak.

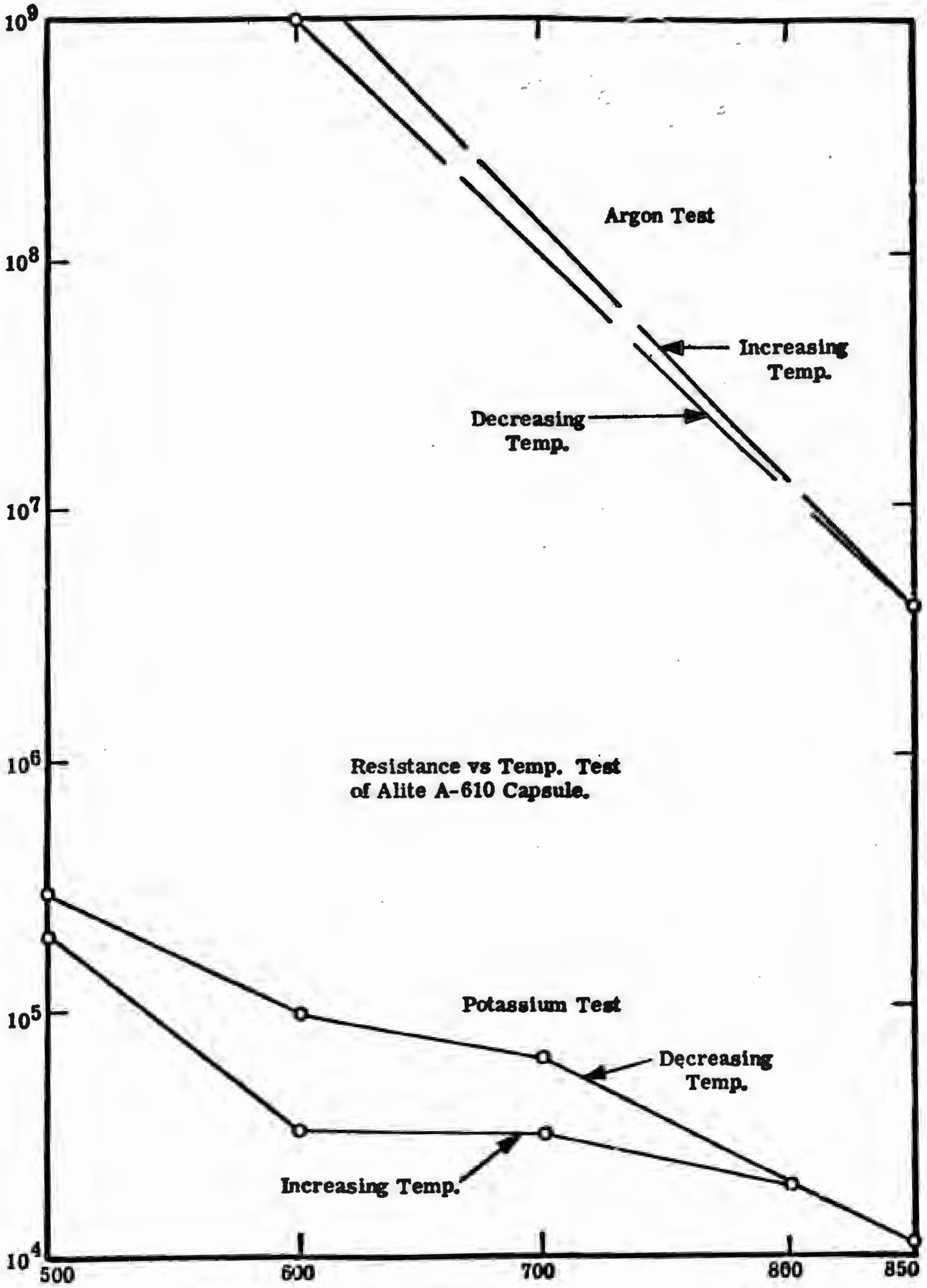


Figure 56. Ambient Temperature, Centigrade

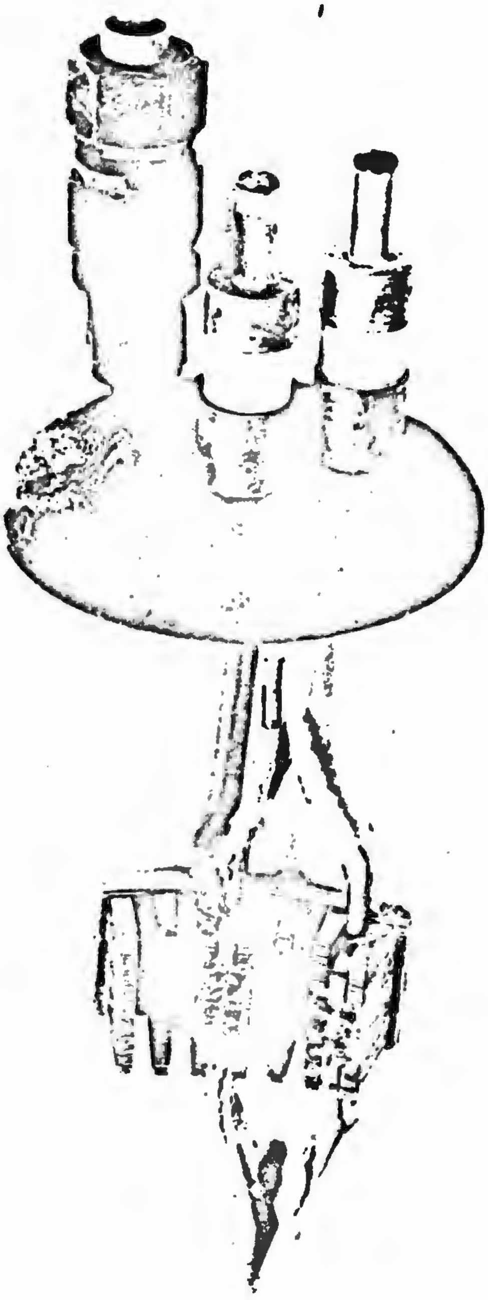


Figure 57. Insulated Coil and Statorette After Potassium Exposure at 850 C

The insulated coils were not electrically tested in mercury vapor at 538 C as no electrical terminal seals resistant to mercury at 538 C were developed during the program.

V. Conclusions and Recommendations

The following conclusions may be drawn from the experimental results.

1. Nickel clad silver and Inconel clad silver conductors have 150 percent of the resistivity of OFHC copper at 850 C. These conductors are resistant to saturated potassium vapor at 850 C for 500 hours.
2. Oxalloy 28, a 410 stainless steel clad OFHC copper conductor, is resistant to 538 C saturated mercury vapor for 172 hours.
3. Ceramic electrical insulators of aluminum oxide, zirconia oxide, aluminum nitride and boron nitride must have a purity greater than 99% for good corrosion resistance to 850 C potassium vapor.
4. Strontium zirconate may contain up to four percent silica as silicon dioxide and still show good potassium vapor corrosion resistance.
5. Ceramic to metal electrical terminal seals can be fabricated, using active metal brazes, that show limited resistance to 850 C potassium vapor.
6. Molybdenum coated nickel clad silver wire can be coated with a potassium resistant ceramic, such as alumina (99%) to form an insulated wire by plasma-arc spraying techniques.
7. Plasma-arc sprayed nickel aluminide can be used to form surfaces to which a ceramic oxide, such as high purity alumina, will adhere.
8. Vapor decomposition of an aluminum chloride-ammonia complex can be used to form an electrical insulation on a metal surface of aluminum nitride that is resistant to 850 C potassium vapor.
9. Nuclear radiation of 10^{19} thermal neutron appears to be detrimental to electrical resistance of plasma arc sprayed insulations such as aluminum oxide or strontium zirconate.
10. No ceramic to metal electrical terminal seals exist at this time that will allow electrical tests to be conducted in potassium vapor for 500 hours.

11. Conventional inorganic potting compounds are not resistant to potassium vapor at 850 C.

Recommendations

It is recommended that more study be given to corrosion resistance of high purity ceramics, development of a good potassium resistant electrical terminal seal, longer life exposure tests of conductors and insulators in potassium vapor at 850 C and actual operation of an electrical device in potassium vapor at elevated temperatures.

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