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**CERAMIC TO METAL SEALS FOR
HIGH-TEMPERATURE THERMIONIC CONVERTERS
Second Quarterly Technical Report**

15 April 1963

Aeronautical Systems Division
Air Force Systems Command
United States Air Force

PROJECT NO. 8173
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(Prepared under Contract No. AF33(657)-10038 by The Bendix
Corporation, Red Bank Division, Eatontown, New Jersey)

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FOREWORD

This report was prepared by The Bendix Corporation, on Air Force Contract AF 33(657)-10038 under Task Number 817305 of Project Number 8173.

This work is being administered under the direction of the Flight Accessories Laboratory, Aeronautical Systems Division. A. E. Wallis is Project Engineer for The Flight Accessories Laboratory.

The report covers the work performed from 1 January 1963 through 31 March 1963, at the Red Bank, Products-Aerospace, and Research Laboratories Divisions of The Bendix Corporation. M. L. Dring is the Project Manager responsible for direction and control of the project.

This report is the second Quarterly Technical Report under Contract AF 33(657)-10038.

This report is unclassified.

ABSTRACT

This report covers work performed in the second three month period of a one year program to develop improved ceramic to metal seals for use in thermionic converters. The objective of this program is to develop seals which are capable of long life at 1500°C in cesium and vacuum environments, and to extend the sealing techniques developed to materials which are capable of long life at temperatures in excess of 1500°C.

Studies are being performed to develop improved methods of sealing both metallized and unmetallized ceramic members to refractory metals. Associated work on ceramics, refractory metal alloys and ceramic-metal composites to provide useful base material characteristics will be carried on as the requirements of the project may dictate.

"The work covered by this report was accomplished under Air Force Contract AF 33(657)-10038, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and simulation of ideas."

1.0 INTRODUCTION

The effort reported here is directed toward raising or eliminating the present operating temperature limits for seal areas of thermionic converter envelope structures by the development of new ceramic to metal sealing techniques. Methods of achieving seals between metallized ceramics and refractory metal members, and between unmetallized ceramics and refractory metal members, are under investigation.

The ultimate temperature goal for materials and seals developed under this project is 2000°C. An interim goal, development of a seal to operate at 1500°C, has been established because of the extreme materials problems associated with use at 2000°C.

Primary attention in this report has been placed on development of techniques for joining molybdenum and high purity alumina. Sufficient success has been achieved with several techniques to justify a high degree of optimism for development of a 1500° seal.

As a result of evaluation of the accomplishments to date, several techniques previously considered feasible will no longer receive attention. Efforts will be concentrated on those techniques on which is placed the greatest expectation of success.

2.0 METALLIZING PROCESS STUDIES

2.1 Work Completed

Six readily available commercial ceramic bodies were selected for use in this study. These bodies have the compositions shown in Table 2-1.

Table 2-1 - Composition of Ceramic Bodies

<u>Body</u>	<u>Alumina</u>	<u>Silica</u>	<u>Magnesia</u>	<u>Calcia</u>	<u>Chromia</u>
I	96.0	3.0	0.5	0.5	
II	99.0		0.25		0.25
III	98.0		2.0		
IV					
V	98.0	1.0			
VI	99.+	0.3			

Body I was selected as a material on which a history of ceramic-metal sealing techniques was known. As such it is being used as the state-of-the-art material against which alumina bodies with higher alumina and lower silica contents can be compared.

Bodies V and VI were dropped from consideration when information became available on the corrosive effects of cesium vapor on ceramic bodies which contained even trace amounts of silica. At the same time, a search was made for other silica-free alumina bodies. Two additional commercially available bodies have been identified which contain 95 and 98 percent alumina, respectively. Lucalox, which is a pressure sintered polycrystalline body containing 99.7 percent alumina and 0.3 percent magnesia, is also being utilized.

Body I, selected for state-of-the-art studies, has a reputation of being difficult to metallize. A strongly adherent coating is difficult to obtain. Flexure tests (see First Quarterly Technical Report¹) showed

¹Ceramic to Metal Seals for High-Temperature Thermionic Converters
First Quarterly Technical Report, pp. 3-4.

metallizing on this body to have marginal adhesion when a standard moly-manganese metallizing slurry was used. Of six tests performed on this combination of materials, two failed at the ceramic-metallizing interface. Similar tests on pieces metallized with a moly-manganese-titanium hydride metallizing showed this combination to have good adherence characteristics. Of twelve pieces tested, none parted at the braze joint. Failure of the piece occurred by fracture of the ceramic beyond the metallizing.

These results were confirmed by tensile tests of standard ASTM pieces of the same body formulation.² Pieces metallized with moly-manganese, sintered at 1550°C, showed an average metallizing tensile strength of 4,300 psi. Pieces metallized with moly-manganese-titanium hydride and sintered at the same temperature showed an average tensile strength of 14,500 psi. Examination of the parted surfaces revealed, on the moly-manganese coated bodies, a white, slightly glazed surface which had been stripped clean of the metallizing layer. Where any coating and solder remained on a piece, it could be easily peeled off with a tweezer and the peeled layer did not appear to remove ceramic. The pieces metallized with the titanium hydride additive slurry revealed a darkened zone on the surface of the ceramic approximately one to two millimeters deep. Metallizing and solder were either tightly adherent to the ceramic, or had torn ceramic from the face of the test piece at the point of rupture.

Table 2-2 lists the results of flexure tests on high alumina bodies which were metallized with various slurries.

As a result of these tests, the moly-cerium and moly-lithium-manganese compositions were dropped from consideration, as was the combination of moly-manganese metallizing on Body II.

Tensile tests, in accordance with ASTM F19-61T, were performed on several bodies using three metallizing slurries. The results are summarized in Table 2-3.

²Tentative Method for Tension and Vacuum Testing Metallized Ceramic Seals -- F19-61T, ASTM Standards, Part 2, p. 1509.

Table 2-2 - Results of Flexure Test

<u>Body</u>	<u>Metallizing</u>	<u>No. of Samples</u>	<u>Results*</u>
II	Mo-Mn-TiH ₂	6	Good
II	Mo-Ti	6	Good
II	Mo-Ce	5	No Good
II	Mo-Li-Mn	5	No Good
II	Mo-Mn	7	No Good
IV	Mo-Mn-TiH ₂	4	Good
IV	Mo-Mn	6	Good
IV	Mo-Ti	5	Good
III	Mo-Mn-TiH ₂	5	Good
III	Mo-Mn	5	Good
III	Mo-Ti	6	Good
I	Mo-Mn	6	4 Good, 2 No Good
I	Mo-Mn-TiH ₂	12	Good

* Good indicates failure in the ceramic.
No Good indicates failure in the seal.

Table 2-3 - Results of ASTM Tensile Tests

<u>Body</u>	<u>Metallizing</u>	<u>Sintering T°</u>	<u>Tensile Strength (Average)</u>
I	Mo-Mn	1550°C	4300 psi
I	Mo-Mn-TiH ₂	1550	14500
II	Mo-Ti	1650	6800
II	Mo-Mn-TiH ₂	1650	4900
III	Mo-Ti	1550	6900
III	Mo-Mn	1550	2570

The effects of the higher temperature sintering of the metallizing on Body II as compared to the temperatures used in metallizing Body III have not been evaluated at this time. More tests will have to be run to arrive at a better statistical position for evaluation. All groups except body I with Mo-Mn-TiH₂ metallizing had some marginal brazes which adversely affected the results.

Figure 2-1 shows the seal area of ceramic Body II metallized with the moly-manganese-titanium mixture and copper brazed. The ceramic, after metallizing, exhibited a dark band adjacent to the adhering metal which extended about one and one-half millimeters into the ceramic. This dark band was not identified but was assumed to be a titanium-containing glassy phase. The dark gray areas in the metallizing are largely a glassy material, assumed to be a reaction product of titanium oxide and the ceramic. It will be noted that the glassy phase has penetrated the metallized layer through its full width to the interface between the metallizing and the copper layer above.

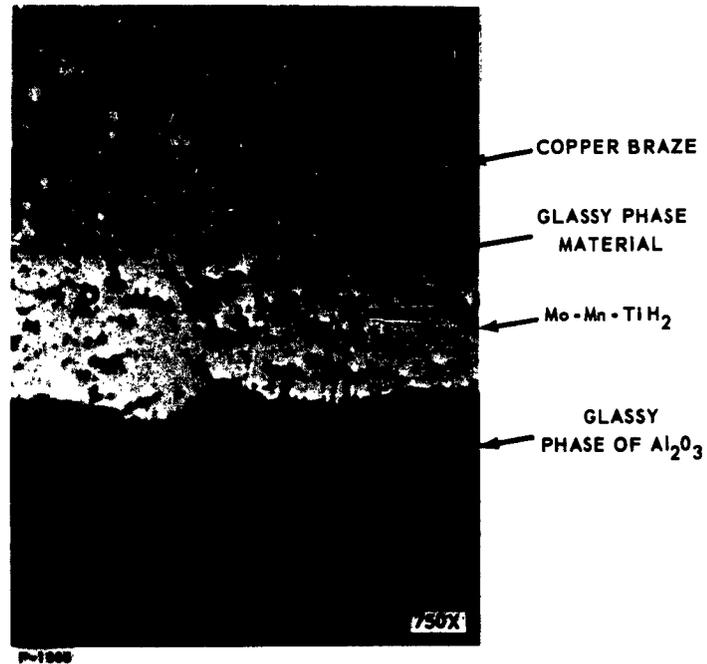


Figure 2-1 - High Purity Alumina Metallized and Copper Brazed for ASTM Tests

An examination of Body II metallized with moly-manganese, disclosed a much smaller reaction zone in the ceramic. This zone, also a dark discoloration, extended not more than 0.1 millimeter into the ceramic and was assumed to be a glassy reaction product of manganese and the ceramic. No interstitial filling of the metallized layer was seen and voids between the ceramic and metallizing were evident.

It is postulated from these observations that, in the titanium-additive metallizing of high alumina ceramics, a rather fluid glassy phase is formed during sintering. This is drawn through the capillaries of the sintered molybdenum compact and, on cooling, freezes to bond the two together. The reaction products of the moly-manganese without titanium and the high alumina ceramic are much less fluid at 1650°C and cannot penetrate the molybdenum layer. Further evidence of this is the fact that in several areas copper which was plated onto the metallizing had penetrated the molybdenum layer and had deposited onto the moly surface adjacent to the ceramic to fill microscopic voids between the two phases. This attempt to explain the mechanism of bonding of metallizing layers to high alumina ceramics (or the reasons for failure to bond) is based only on the evidence obtained from microscopic examination. These hypotheses could be proven or substantiated only by a long program of positive identification of the reaction products. Synthesis of the observed glassy phase in a reducing atmosphere at the temperature of sintering, and measurement of the viscosity of the melts produced, could also be possible approaches to the proof of the theory.

A piece of single crystal sapphire, one-quarter inch in diameter and approximately one-quarter inch high, was metallized with the moly-titanium slurry sintered at 1650°C, and copper brazed to copper plated molybdenum. The seal was effected at 1150°C and proved to be an excellent bond. Micrographic studies of a section of the seal provided evidence of a glassy phase which had penetrated the metallizing layer in a manner similar to that shown in Figure 2-1.

2.2 Plans for Next Quarter

The newly identified high purity bodies will be evaluated to determine the specific requirements of these for high strength metallizing. Additional ASTM type tests will be performed to enable a statistical evaluation to be made of the metallizing strength.

3.0 BRAZING STUDIES

3.1 Work Accomplished

Sapphire rod and high purity alumina wafers, metallized with a molybdenum-titanium slurry, were successfully brazed to unplated molybdenum sheet stock. Both iron powder and cobalt powder were used as the brazing media. The resulting bonds were excellent. However, the ceramic members of the joints formed were found to be cracked after processing with either brazing filler.

Since butt-braze joints are inherently weak to resist the stresses developed during processing with materials of sharply differing coefficients of expansion, the ceramic failures are attributed to this cause.

Brazing trials using a strip of 50/50 nickel-iron as a solder resulted in the nickel stripping the metallizing from the ceramic. No joint was accomplished.

3.2 Plans for Next Quarter

High temperature brazing material studies will be continued, with emphasis on identifying useful braze materials with suitable coefficients of thermal expansion.

4.0 ELECTRON BEAM WELDING STUDIES

4.1 Work Completed

The problem of suitable fixturing for holding the ceramic and metal components together during butt-welding trials was overcome by proper weighting of the components. Butt welds were made between 96 percent Al_2O_3 , sapphire, and lucalox as the ceramic members and columbium and tantalum. In all cases fusion was obtained, however, neither mechanically strong nor hermetic seals resulted. Fine transverse cracking occurred in the ceramic members. No transition area was formed in which transition or reaction products promoted formation of a bond.

In order to study the reactions between alumina (the ceramic of major interest in this investigation) and the refractory metals, small crucibles of tungsten were fabricated into which were packed chips of 96 percent alumina interspersed with chips of a refractory metal. Columbium, tantalum, molybdenum and tungsten were utilized. The chip size was approximately $1/16'' \times 1/8''$. These filled crucibles were then placed in the electron beam vacuum chamber and, after pumpdown and preheating, the contents of each crucible was completely fused by impingement of the electron beam. Each crucible was then embedded and sectioned. Photomicrographs showed that no usable interface had resulted in any of the crucible welds.

It may be concluded from these studies that although fusion does take place between the metal and ceramic in each case, upon cooling there exists no gradation of phases from the ceramic to the metal such that the differing expansion coefficients are matched or blended. Thus, cracking results. No reaction products are formed which promote bonding.

Metallized 94 percent alumina cylinders were electron beam welded to molybdenum with the beam normal to the plane of the molybdenum disk. Control of the electron beam power was inadequate. The beam melted the glassy phase of the ceramic which then flowed between the molybdenum and the alumina forming a bond of a different nature than that intended and not of useful value.

Control of the generated heat and the penetration depth of the beam were studied by electron beam welding a 0.015" molybdenum sheet to 0.001" molybdenum foil on an alumina support. The thick molybdenum sheet has been successfully welded to the foil without cracking or marring the alumina support. It is, therefore, concluded that a hermetic seal can be formed between a metallized ceramic and metal member by this technique. However, glass-bearing aluminas are less desirable in this application because the glass melts before a metallurgical weld can be made. With a beam of the proper penetration a weld should be possible between molybdenum and metallized glass-free alumina.

4.2 Plans for Next Quarter

Studies on the welding of molybdenum sheet to metallized alumina will be continued. The primary attention will be given to surface preparation of the metallizing and molybdenum sheet and to determining welder control parameters which will enable successful control of beam penetration.

5.0 ULTRASONIC WELDING STUDIES

5.1 Work Completed

Study of the specimens from the first series of tests, conducted at the Sonobond Corporation laboratories in December, 1962,¹ has indicated that a weld could be produced between 0.001" molybdenum sheet and alumina metallized by conventional methods. However, the following general problem areas have been identified by this study:

- (1) The need for a material for use as welding tips that would reduce the galling and metal transfer during welding that was experienced when DBL carbon alloy tips were used.
- (2) The difficulty of welding appears to increase greatly with increase in thickness of molybdenum sheet.
- (3) Increase in power and contact pressure improve welding of molybdenum, however, the mechanical shock resistance of the alumina may be exceeded before acceptable welds can be made when relatively thick molybdenum (0.010" to 0.025") is used.

Metallographic study of specimens from this first series of tests showed that the use of a 0.0005" tantalum foil interleaf between the molybdenum sheet and the metallized surface greatly improved weld conditions. Figure 5-1 is a photomicrograph of a weld area showing the weld integrity that can be obtained using tantalum foil interleaf.

Because of the metal transfer problem, welding tips were constructed from Udimet 700 (Ni base alloy). This alloy was recommended as one of the best materials available to reduce the galling or metal transfer problem. Since the earlier tests had also indicated that use of a welding tip with a smaller radius might improve the weld, new tips were made with 2", 1.5", and 1" radii. It was believed that it might

¹ Reported in detail in the First Quarterly Technical Report under this contract, 15 January 1963.

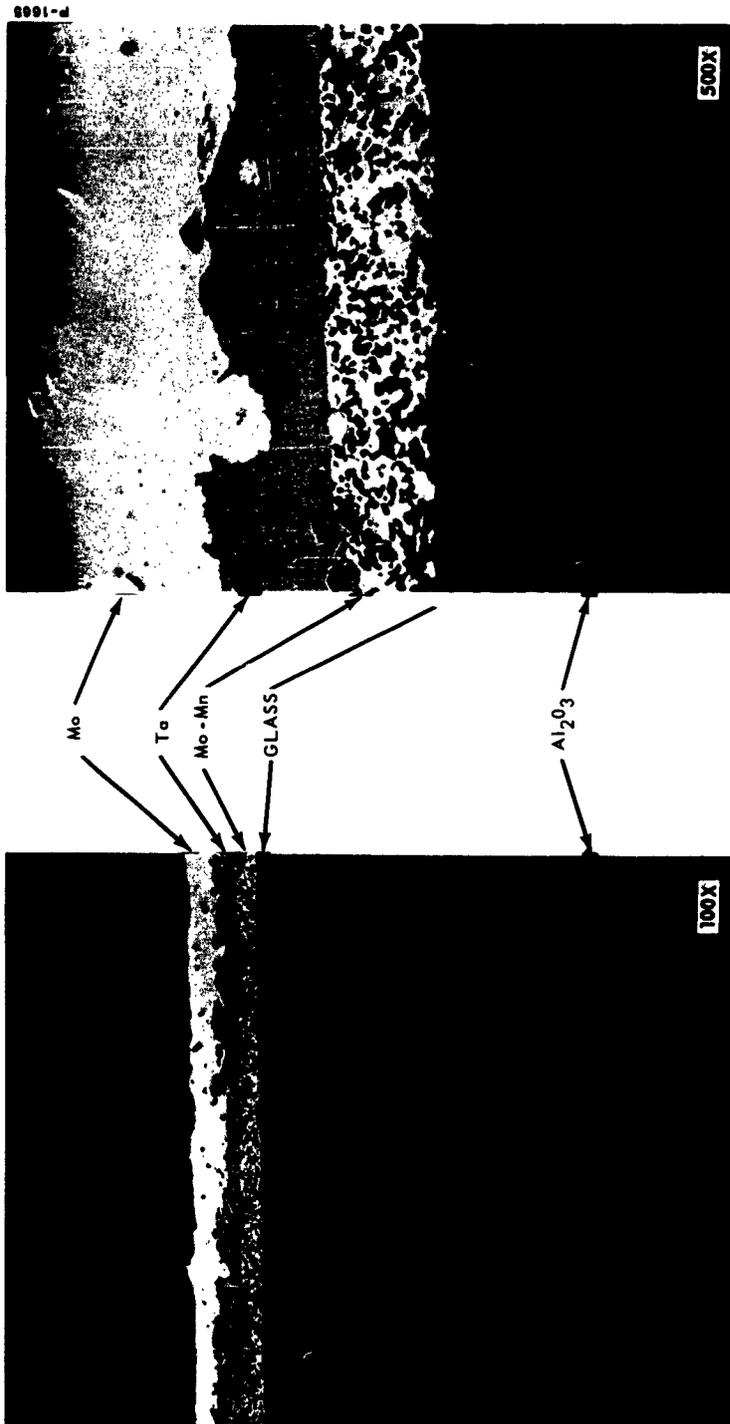


Figure 5-1 - Ultrasonic Weld of Molybdenum to Alumina
with Tantalum Interleaf

be possible to increase contact pressure by this method without exceeding the mechanical shock strength of the alumina. These changes in welding tip material, and configuration did improve results obtained in the second series of tests. However, pick-up or metal transfer was not completely eliminated and welds made by using the smaller radius tips were broken during the next weld due to metal deformation.

The preliminary results of the second series of tests are summarized as follows:

- (1) Some reduction in galling tendencies was obtained through the use of Udimet 700 alloy tips. However, the improvement was not sufficient to warrant consideration of this material for any kind of production tooling.
- (2) There is a definite improvement in the weldability of the components when a tantalum foil interleaf is used.
- (3) The weakest interface in the system appears to be the bond between the metallized coating and the alumina.
- (4) Visual examination showed no fractures of the Molybdenum during welding.

The following tentative conclusions have been drawn from the results of the studies made to date:

- (1) It appears feasible to consider welding molybdenum sheet in 0.005" - 0.010" thicknesses to metallized alumina if thermionic converter designs can use materials of this thickness.
- (2) Welding of thicknesses of Molybdenum or molybdenum alloys exceeding 0.010" to metallized alumina is extremely doubtful with state-of-the-art ultrasonic welding.

5.2 Work Planned for Next Quarter

The specimens from the second series of tests will be subjected to metallographic examination. If fractures are found in the weld bead area during metallographic examination, the possible usefulness of heating the components to a temperature above the transition temperature of molybdenum prior to or during the welding operation will be carefully evaluated.

The results of studies performed to date will be carefully evaluated to establish specific objectives for additional work in this task, or to determine whether activities in this task should be discontinued.

6.0 ELECTROFORMED SEAL STUDIES

6.1 Work Completed

Successful plating of rhodium on a brass substrate to thicknesses in excess of 0.0035" was reported in the previous Quarterly Technical Report. Electroplating of rhodium on molybdenum has been found to be more difficult than on brass because of cracking due to the development of high stresses in the plated rhodium. Although the stress conditions also exist in the rhodium plated on a brass substrate, the effect is not as serious. A better bond is formed between the brass and the rhodium. Figure 6-1 is a photomicrograph indicating the degree of cracking and separation exhibited by electroplated rhodium on molybdenum.

The use of an intermediate layer of electroplated chromium or nickel was considered as a possible means of improving the bond when plating rhodium on molybdenum. Plating trials using these intermediate materials were unsuccessful. Neither nickel nor chromium gave evidence of improving the bond of rhodium plated on a molybdenum substrate.

Stress-relieving thermal treatments were considered as a processing step which might be used to reduce the effect of the highly stressed plated coatings. Plated specimens were annealed in vacuum for periods up to one hour at 540°C and 980°C. Annealing at 540°C was not effective in reducing stress cracks; however, annealing at 980°C eliminated essentially all coating discontinuities. A section of a plated sample annealed in this manner is shown in Figure 6-2a. An additional 0.001" of rhodium was then plated on the sample shown in Figure 6-2a. After a final annealing at 980°C, this specimen was again sectioned. The section is shown in Figure 6-2b. The plated material shows excellent adhesion and good coating integrity.

Plating of rhodium over a lap-joint between two sheets of molybdenum was considered the next step toward accomplishment of an electroformed ceramic-metal seal. This presented the following additional problems:

- (1) How to join the materials together prior to plating.

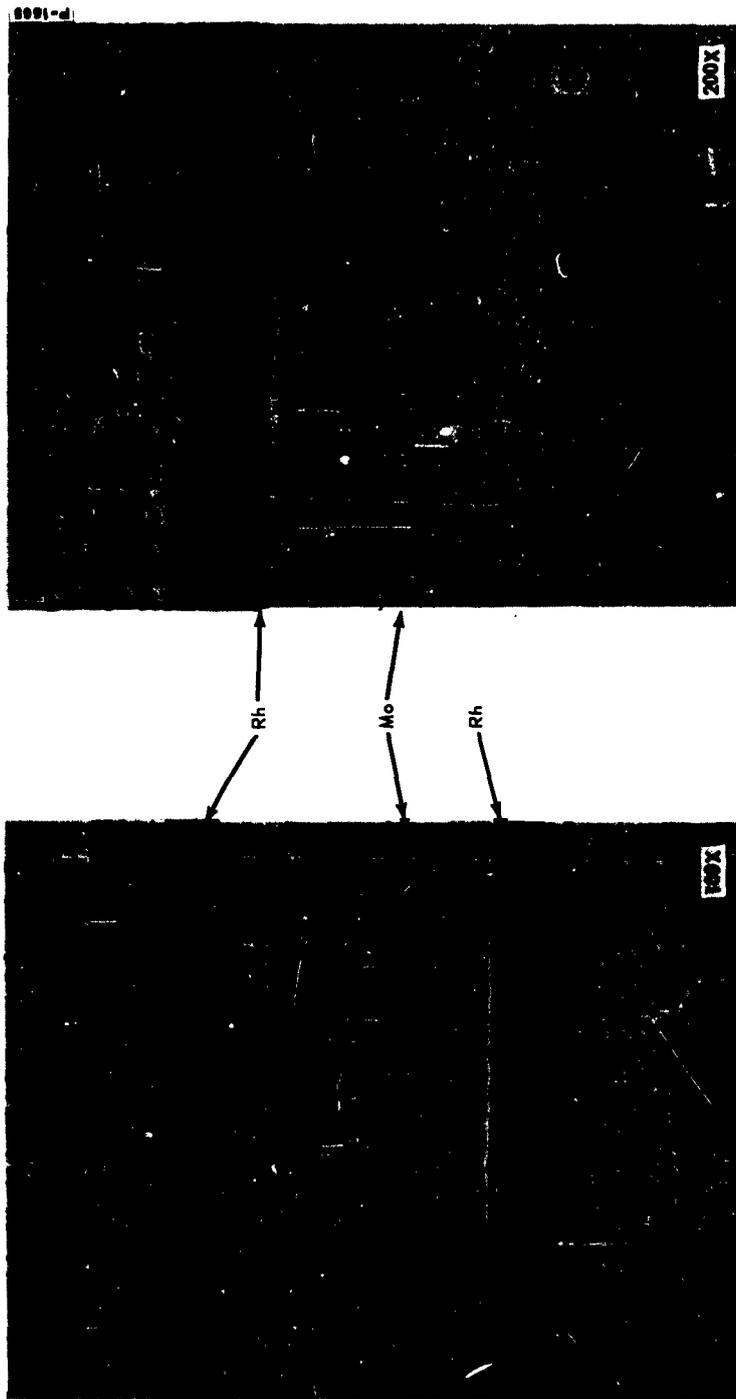
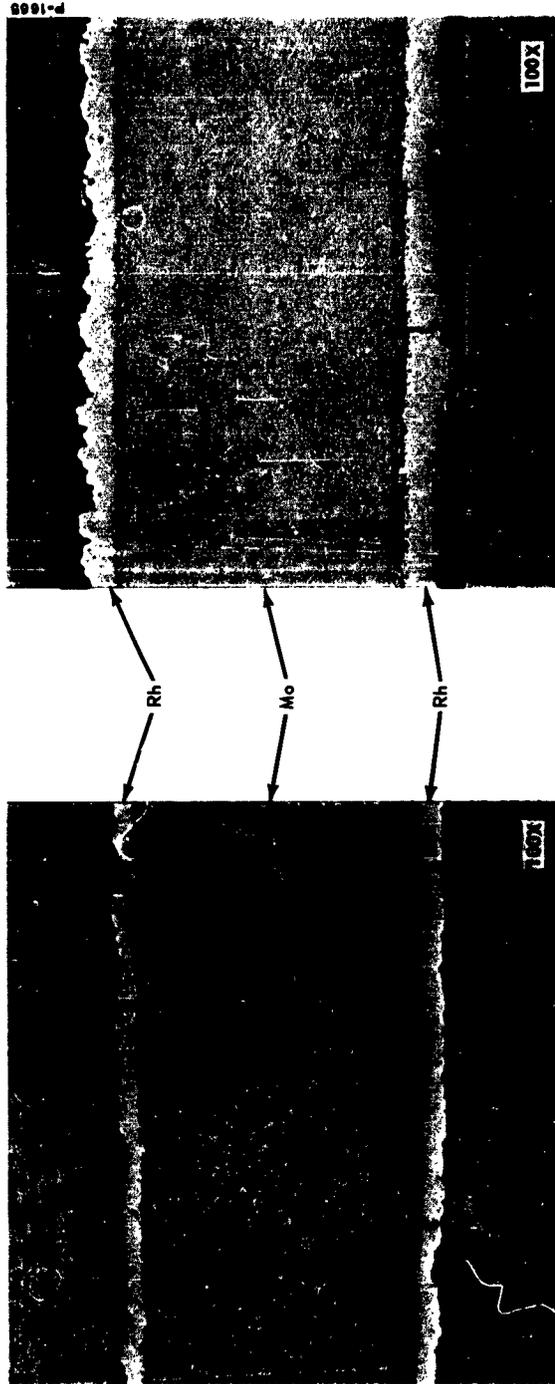


Figure 6-1 - Electroplated Rhodium on Molybdenum Sheet



(a) - 1 Plating Cycle

(b) - 2 Plating Cycles

Figure 6-2 - Electroplated Rhodium on Molybdenum - 980°C
Stress-Relief Anneal

- (2) How to eliminate seepage of plating solution into resulting crevice between sheets.
- (3) How to form joint so that a continuous plated surface would result spanning the lap joint.

Molybdenum sheets were joined together by spot welding using an organic lacquer to fill the space between them. The upper sheet was beveled at approximately a 30° angle to minimize the step at the junction of the two sheets. Several specimens of this configuration were plated with approximately 0.0015" of rhodium. Figure 6-3 is a photomicrograph of a cross-section of one of these lap joints. It can be seen that plating over this type of joint is possible, however, the difficulties which must be overcome before a hermetic closure is obtained are formidable.

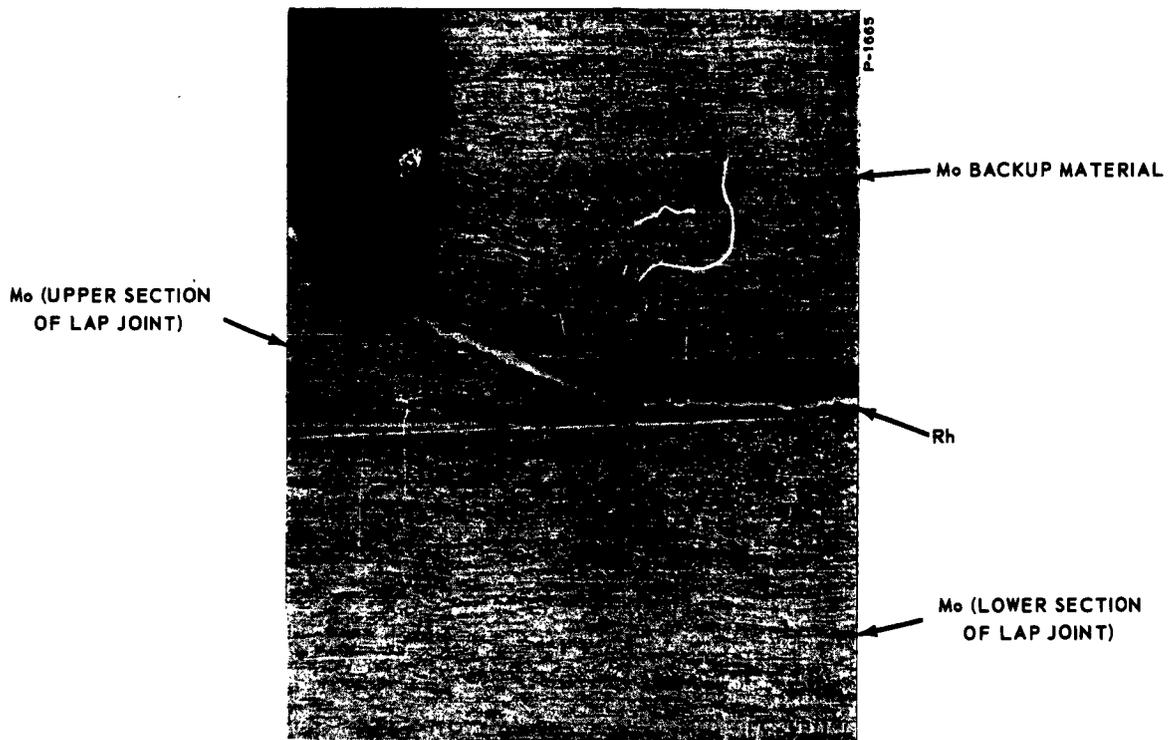


Figure 6-3 - Electroplated Rhodium Over a Lapped Joint between Two Sheets of Molybdenum

The electroplated rhodium concept is still considered to be a feasible approach to obtaining a high temperature seal. However, the practical problems which must be overcome in developing the necessary techniques indicate that it will be more difficult to prove out this concept than others still under active consideration. Therefore, no additional work is planned on this study. The experience gained in plating rhodium should also be applicable in plating rhenium if the use of this material as an emitter surface or a potential electroformed seal is desirable.

7.0 DIFFUSION SEAL STUDIES

7.1 Metal to Oxide Studies

The initial phase of this program has as its goal the development of a seal for use up to 1500°C. The basic materials of this study are molybdenum and silica-free alumina. Some of the systems that have been proposed as means of producing seals are shown below with desired transition zone reaction products indicated by parenthesis:

1. Mo (Mo·Cr) Cr·MgO (MgO·Al₂O₃) Al₂O₃.
2. Mo (Mo·Cr) Cr₂O₃ (Cr₂O₃·Al₂O₃) Al₂O₃.
3. Mo (Mo·Mg) MgO (MgO·Al₂O₃) Al₂O₃.
4. Mo (Mo·Mg) Mg (MgO·Al₂O₃) Al₂O₃.
5. Mo (Mo·Ni) Ni (NiO·MgO) MgO (MgO·Al₂O₃) Al₂O₃.
6. Mo (Mo·Cr) Cr (Cr₂O₃·MgO) MgO (MgO·Al₂O₃) Al₂O₃.
7. Mo (Mo·Cr) Cr (Cr₂O₃) Cr₂O₃ (Cr₂O₃·Al₂O₃) Al₂O₃.
8. Mo (Mo·Ni) Ni (NiO·Al₂O₃) Al₂O₃.
9. Mo (Mo·Mn) Mn (MnO·MgO) MgO (MgO·Al₂O₃) Al₂O₃.
10. Mo (Mo·Mn) Mn (MnO·Al₂O₃) Al₂O₃.

Several methods of obtaining these reactions have been considered. These include control of atmosphere during heating using vacuum, hydrogen, and inert gases for example. The reactive materials may be introduced by various means such as loose powders, flame spray, arc-plasma spray, or vapor deposition.

A number of specimens were prepared with the reactive materials introduced by these means. These specimens were heated in vacuum for 9 hours at 1620°C with approximately 8 psi load. Higher loading would be desirable; however, the limitation of the furnace made greater loads impractical at the time. The first test series consisted of heating molybdenum and alumina flat stock with the following powders between them: MgO, Cr₂O₃, and Cr-MgO composite (85 volume percent Cr, 15 volume percent MgO). The result of this series indicated that reaction

had occurred between the following materials: Mo and Cr, MgO and Al₂O₃, and Cr₂O₃ and Al₂O₃. There was no evidence of continuous bonding between the molybdenum and alumina by any of these reactions but the fact that reactions were accomplished under the heating cycle indicated that a bond may be realized by the proper combination of reactive materials.

A second series of tests was made using specimens prepared as follows:

1. Molybdenum on which was plasma sprayed Cr-MgO Composite; in contact with alumina.
2. Molybdenum on which was plasma sprayed Cr₂O₃; in contact with alumina.
3. Molybdenum on which was plasma sprayed MgO; in contact with alumina.

Results of the second series of tests correlated well with the first test series in that no bond was produced between the molybdenum and the alumina; however, metallographic examination indicated that:

1. Chromium from the Cr-MgO composite reacted with the molybdenum to form a tight metallic layer on the surface of the molybdenum as shown in Figure 7-1. This metallic layer is believed to be a chromium-molybdenum alloy.
2. Chromium oxide (Cr₂O₃) reacted with molybdenum to form a metallic layer similar to that produced by the Cr-MgO composite except that the alloy layer is thinner. Figure 7-2 shows a cross-section of this specimen.
3. MgO was completely removed from the molybdenum however, there was a definite reaction between MgO and the alumina as shown in Figure 7-3.

A third trial was made to study system #5 of the first paragraph. In this system the molybdenum sheet was coated with flame sprayed (oxy acetylene) nickel, and the alumina was coated with arc-plasma sprayed MgO. This system produced a bond which withstood considerable handling. A metallographic study of this specimen indicated definite reaction areas as shown in Figure 7-4. There is a tight layer of nickel-molybdenum alloy on the molybdenum which is interlocked with a ceramic phase believed to be NiO. There appears to be MgO intermixed with the NiO. Micro-hardness test results on this system are shown in Table 7-1.

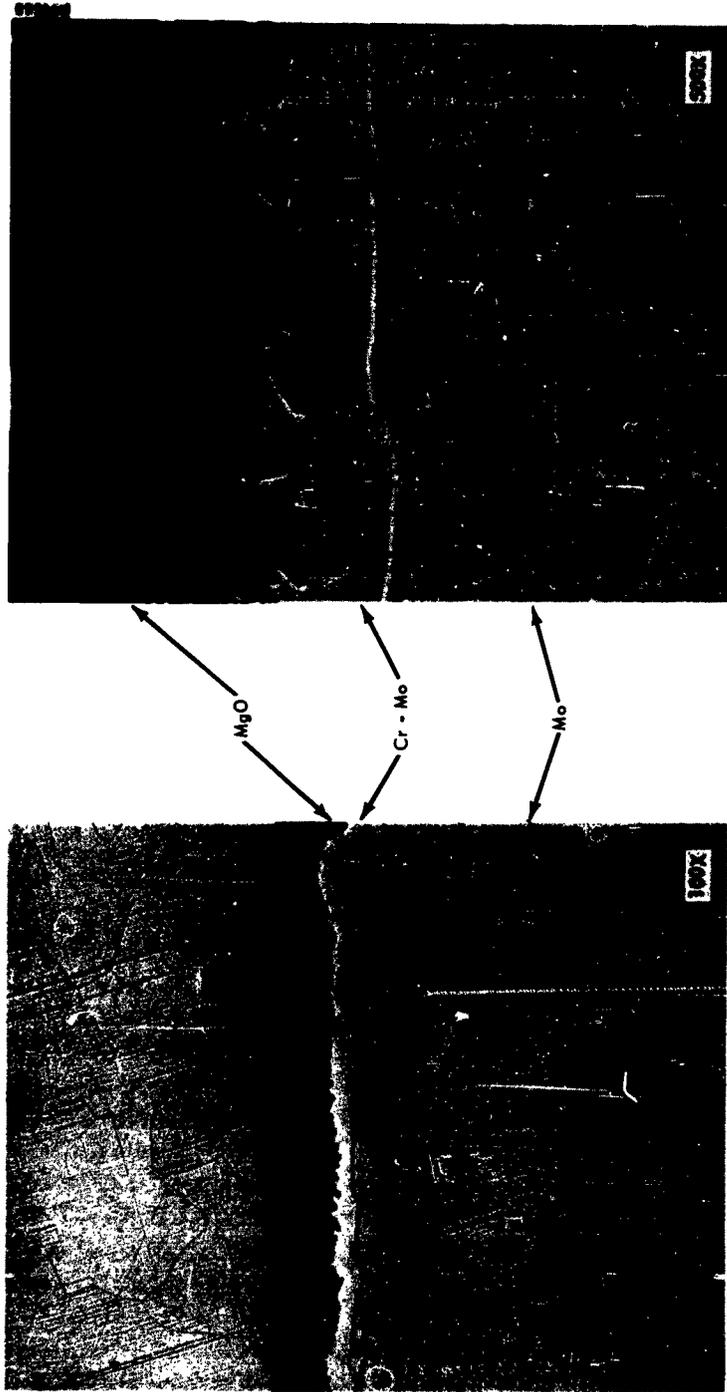


Figure 7-1 - Plasma Sprayed Cr-MgO Composite on Molybdenum Heated in Contact with Alumina

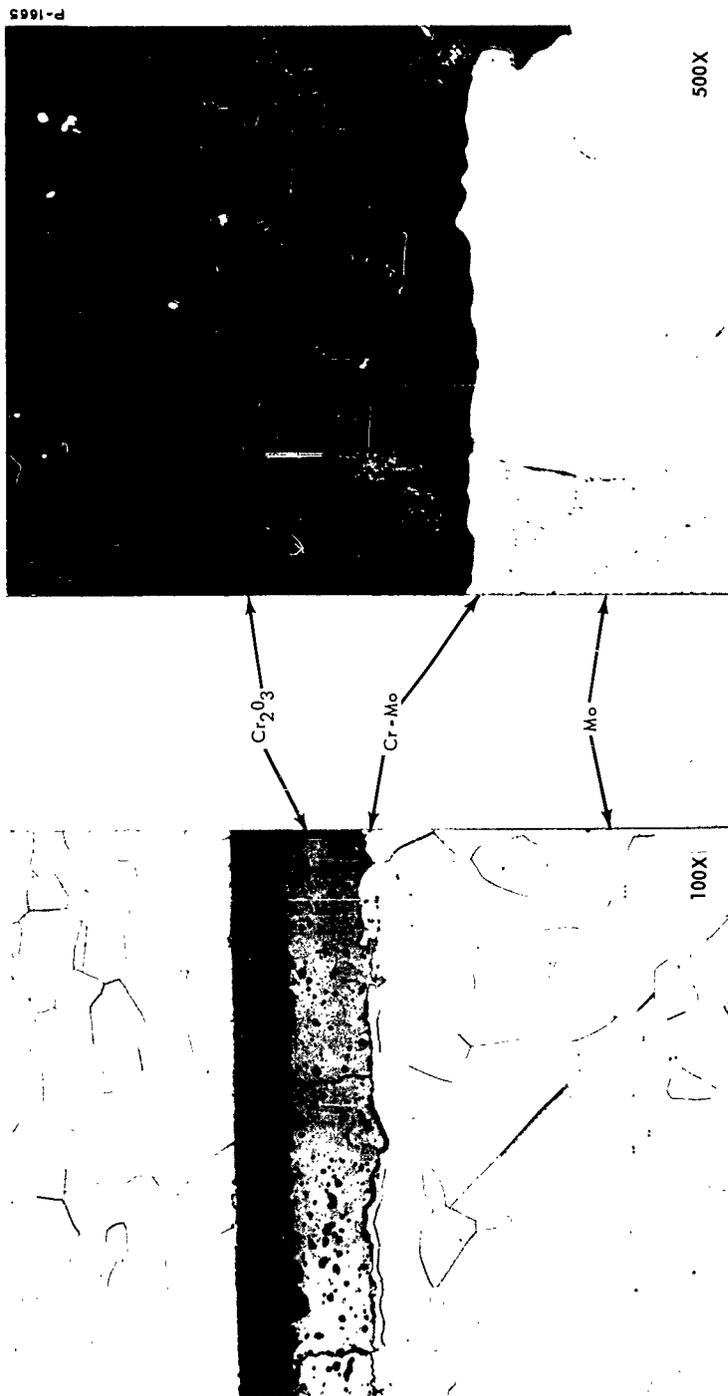


Figure 7-2 - Reaction Between Molybdenum and Chromium Oxide
(Chromium Oxide Plasma Sprayed on Molybdenum and Heated
in Contact with Alumina)

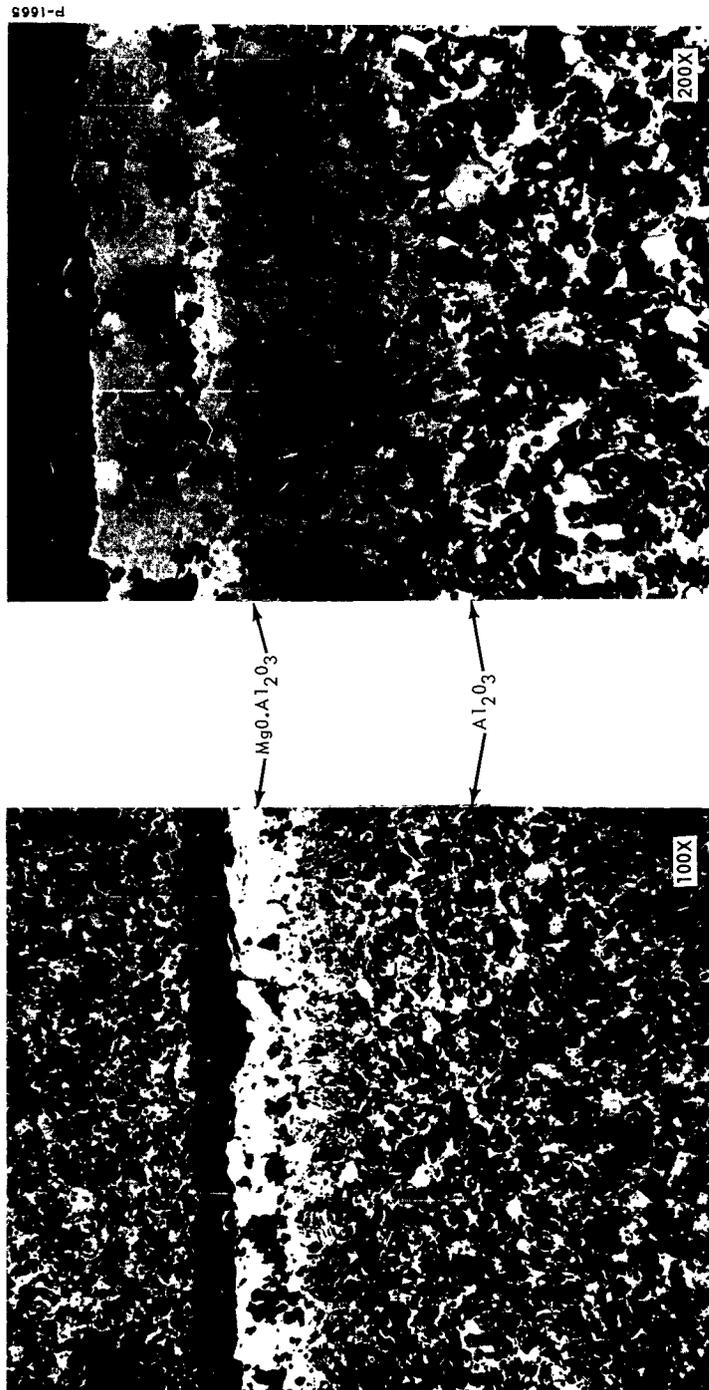


Figure 7-3 - Reaction Between Al_2O_3 and MgO (MgO Applied to Molybdenum Sheet and Heated in Contact with Alumina)

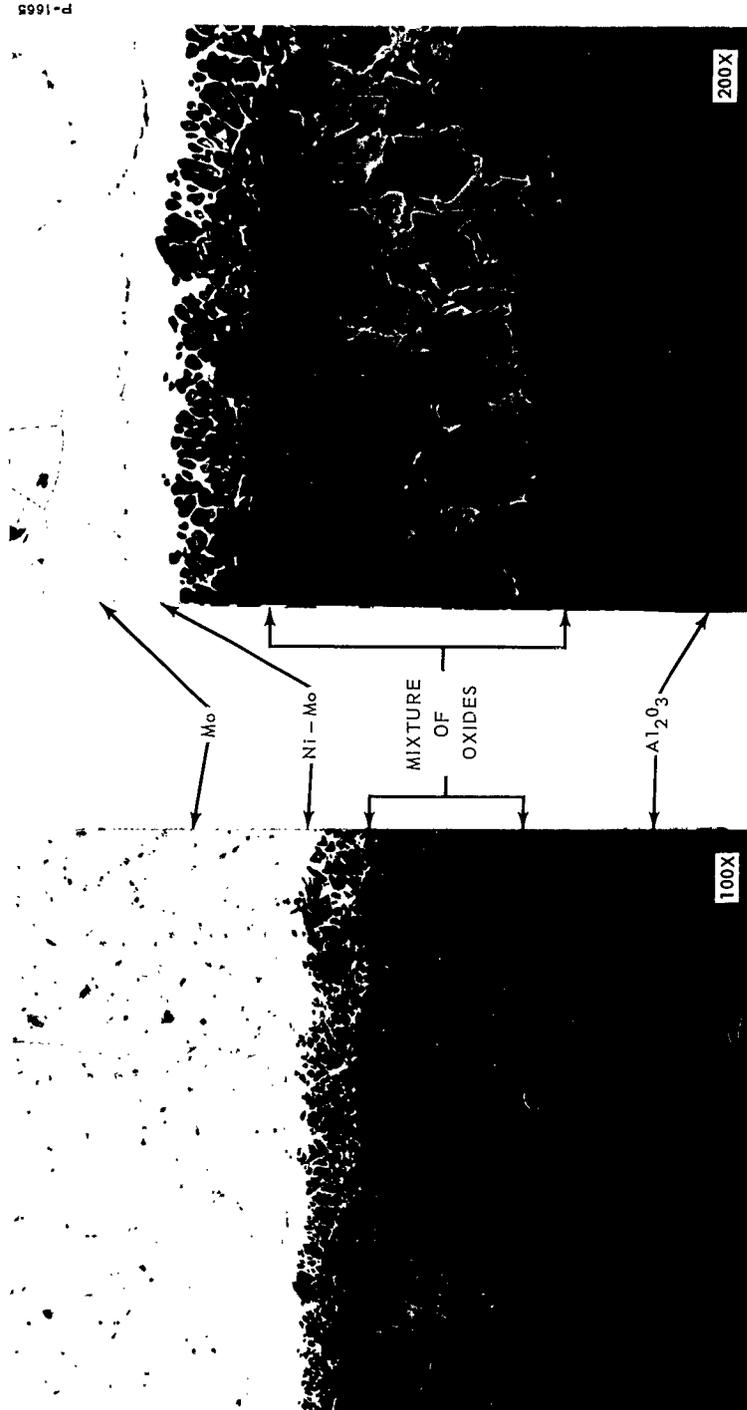


Figure 7-4 - Diffusion Joint between Molybdenum and Alumina

Table 7-1 - Micro Hardness Data on Diffusion Joint of Figure 7-4

<u>Phase</u>	<u>Knoop Hardness</u>
Al ₂ O ₃	1693
NiO-MgO	1094
Ni-Mo Alloy	402
Mo	170

7.2 Metal to Metal

Chromium is an active, rapidly diffusing metal which forms a complete series of solid solutions with molybdenum. Also, chromium oxide forms a complete series of solid solutions with alumina. Therefore, chromium appears to be a good addition to molybdenum to promote sintering at lower temperatures. Since chromium is the same group of the periodic table as molybdenum the same bonding mechanism or adhesive forces may be operative for chromium as for molybdenum.

Slurries of molybdenum and chromium powders were prepared as metallizing mixtures. They adhered well to the alumina and could be polished to a bright luster. The metallizing mixture also adhered well to molybdenum sheet.

A metallizing surface was prepared on silica free alumina using 80 Mo - 20 MnO₂ or 85 Mo - 10 Mn - 5 TiH₂ fired at 1600°C for 1/2 hour in argon. The moly grains became embedded in the ceramic when the MnO - Al₂O₃ eutectic melted and flowed into the interstices between the grains. For diffusion studies a two layer separately fired metallizing procedure was used. The second layer was 80 Mo - 20 Cr. This layer was also fired for 1/2 hour at 1600°C in argon.

The metallized surfaces were lapped and polished through 1 micron alumina abrasive and placed in contact with molybdenum sheet. Pressures of up to 210 psi were applied and the specimens were fired at 1600°C for up to 2 hours in argon.

In the specimen prepared with this procedure the joint was adherent but non hermetic. Also the alumina cylinder cracked, presumably from non-uniform loading during processing. Processing at a pressure

of 7.6 psi and a time of 2 hours also produced a strong but non-hermetic seal. The seals were strong as evidenced by the pulled grains when the bonded molybdenum was stripped off the alumina.

In such a joint, the metallized layer almost completely diffuses into the molybdenum. The degree of intimate contact, lack of voids and general appearance of the bond indicates that a hermetic seal should be possible with this technique. There is a large number of variables that must be optimized in order to form a hermetic seal. They are:

1. Surface preparation
 - (a) of molybdenum sheet
 - (b) of alumina surface
 - (c) of metallized surface
2. Layer composition
3. Metallizing layer thickness
(Number of separately fired layers)
4. Pressure
5. Firing temperature
6. Firing time

Since the metal-to-ceramic bond is of both a chemical and mechanical nature the preparation of the alumina surface before metallizing may be of importance. A rougher surface would provide more contact area as well as a mechanical locking between metal and ceramic. This could be accomplished by abrading or etching the surface.

The molybdenum sheet was used as received, only cleaned with alconox, water and acetone. The metallized layer was lapped flat and polished through Linde C, 1 micron alumina abrasive. Results would indicate that this treatment is sufficient.

It is necessary to paint at least two layers of metallizing slurry. One layer cannot be made thick enough to lap and polish without cracking on firing. Since it has been found that a Molybdenum-chromium layer sinters to moly better than a moly manganese and the latter bonds well to alumina a multilayer metallizing may be desirable.

Pure molybdenum adheres only weakly to alumina. It can be scraped off with a sharp blade and cannot be polished: Both 80 Mo -

20 Cr and moly-manganese layers such as 80 Mo - 20 MnO₂, 85 Mo - 10 Mn - 5 TiH₂ adhere well and can be polished to a fine finish. However the 80 Mo - 20 Cr will bond to molybdenum well because of the concentration gradient and the high diffusivity of chromium.

A high pressure is necessary for a good hermetic bond. The disadvantage of high pressures is the tendency to cause cracking of the ceramic. The maximum pressure that will not crack the alumina remains to be found.

1600°C has been found to be a satisfactory firing temperature for the various metallizing mixtures. At lower temperatures, the particles of the slurry do not sinter together and the layer cannot be polished. At higher temperatures the added constituents such as MnO and Cr vaporize out of the metallizing mixture. Firing at high temperatures to eliminate the low melting materials may be a good way to increase the working temperature of the seal. The pressure sintering temperature has also been 1600°C so that chromium would not be lost by vaporization. It may be necessary to go to higher temperatures in order to form a hermetic seal.

Firing time of 1/2 hour has been used to metallize alumina. Shorter times may be sufficient. Various firing times, as high as two hours have been used in pressure bonding without forming a hermetic seal. The shortest time that would form a hermetic seal would be desirable.

7.3 Work Planned for Next Quarter

The various proposed systems listed in the beginning paragraph of Section 7.1 which have not yet received detail attention will be screened to identify systems which show promise. Promising systems will receive a thorough study to determine their capabilities of producing usable bonds. Strength tests will be performed on specimens prepared using the systems which show greatest capabilities. These strength tests will be made in accordance with ASTM F19-61T to provide a basis of test standardization. Those systems that exhibit good bonding and relatively tight structural integrity will be used to seal the molybdenum to the alumina cylinder of Figure 7-5. These assembled units will then be tested for vacuum tightness and thermal shock resistance.

A hermetic seal by pressure bonding molybdenum to metallized alumina will be made by finding the optimum surface preparation,

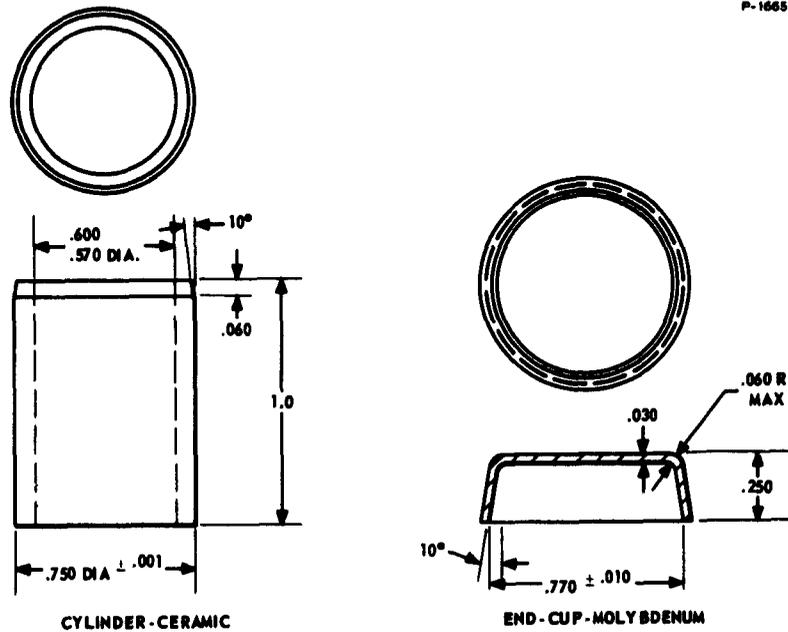


Figure 7-5 - Seal Evaluation Sample

metallizing layer composition, layer thickness, pressure, firing temperature, and firing time. A better method of applying pressure than that presently used will be sought so that weight can be more evenly distributed over the entire bonding surface because of the non-hermeticity and cracks that have occurred due to stress concentrations in uneven loading.

8.0 COMPOSITE ENVELOPE STUDIES

8.1 Work Completed

The objective for this period of the program was to fabricate a composite cup-shaped envelope graded from tungsten to alumina. The two methods considered for forming the cup were plasma spray forming and hydrostatic pressing.

Studies, reported in the first quarterly report, had enabled suitable particle size, lubricant additions, bonding materials, and sintering aids to be determined. The general steps required to make a cup-shaped envelope were determined to be:

- (1) Loading of die with graded material.
- (2) Pressing.
- (3) Presinter (if necessary for machining).
- (4) Machining.
- (5) Sintering.
- (6) Final Machining.

Prior experience has shown that hydrostatic pressing is superior to die pressing since parts with more uniform density can be obtained by this method. It had been determined by die pressing studies that the optimum pressure for pressing tungsten was in a range of from 15,000 to 20,000 psi. The optimum pressure for pressing alumina was from 40,000 to 50,000 psi. The hydrostatic press normally used for this type of work in the laboratory has a maximum working pressure limitation of 20,000 psi. For this reason it was decided to do the early pressing studies using the die pressing facilities. When grading, machining and sintering problems had been thoroughly studied, a method of hydrostatic pressing with greater pressures would be made available.

Employing die pressing techniques, methods of grading incrementally and by infinite gradations were studied. Also studied during this period was the effect of moisture on pressing and on green strength. Addition of moisture presented a problem in some cases since damp powders could not be metered through the powder feeding equipment when infinite

grading was being studied. Normally, powder and moisture were blended together prior to loading into the die; however, when the powder feeding equipment was used it was necessary to add moisture after loading. Studies of machining techniques resulting in procedures by which billets that have substantial green strength could be satisfactorily machined without a presinter.

Several parts that had been machined from die pressed billets were sintered with relatively little variation in shrinkage from the tungsten area to the alumina area. These parts did have some laminations and variation in density due to the use of the die pressing technique. Figure 8-1 shows a cross-section of one of the sintered composite envelopes using incremental grading.

8.2 Plans for Next Quarter

Efforts will be directed at obtaining vacuum-tight infinitely graded composite envelopes by the use of pre-compacted powders and hydrostatic pressing at pressures up to 100,000 psi.

Up to the present time, the fact that moisture has been required to obtain a substantial degree of green strength has limited the use of the powder feeders for obtaining an infinitely graded structure. The moisture problem may be overcome by the use of the pre-compacted powders. These powders would then be granulated to a desired size for use in the powder feeding equipment. The use of a binder, such as polyvinyl alcohol, in the pre-compacted powders may aid in the compacting so that satisfactory compacts could be made with little or no moisture addition. Under these conditions the use of the powder feeders for obtaining infinitely graded structures would be feasible.

Although the use of arc-plasma spray equipment is another potential method of producing a composite structure, a thorough study of this method has been postponed until later in the program. Some of the reasons for this postponement are listed below:

- (1) The arc-plasma spray process is relatively inefficient in terms of time and material when compared with pressing and sintering. For this reason it was considered more logical to first study the pressing method and keep the spray forming process as an alternate method for later study, if pressing techniques were not feasible.

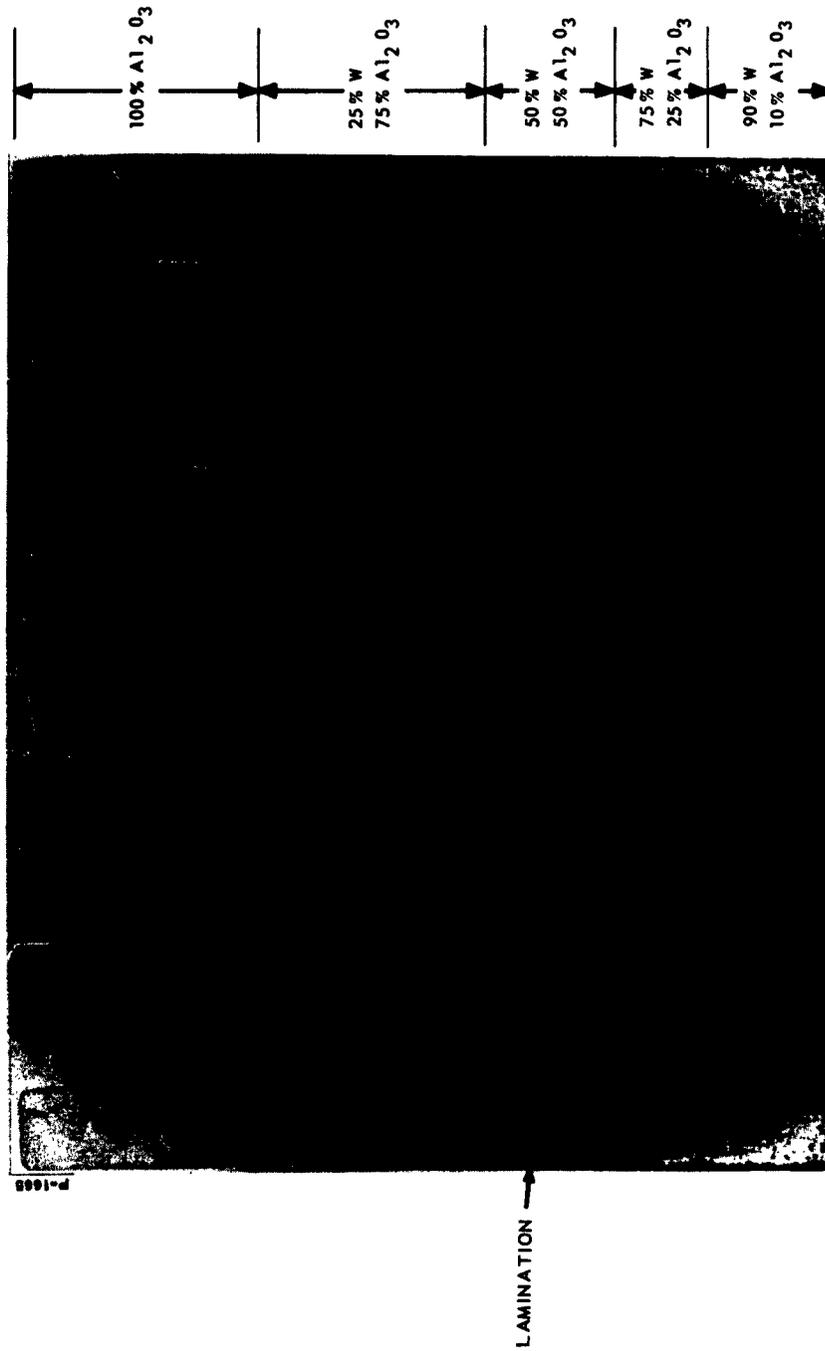


Figure 8-1 - Cross Section of Sintered Composite Envelope

- (2) Because of the oxidation problem inherent in the use of refractory metals, the use of an argon atmosphere should be considered when spray forming the composite structure. As a controlled atmosphere spray booth is not now available, it is believed that this portion of the work should be postponed until this facility can be made available.
- (3) The inefficiency that arises from continually moving the powder feeding equipment from one area to another seems to justify the completion of the study of one potential method before starting on another.

9.0 MATERIAL STUDIES

9.1 Oxide Systems

X-ray studies have been completed on the system thoria-erbia. The study confirms a complete solid solution system between the two components. This means that potentially detrimental eutectic formations or compound formations are absent and that $\text{ThO}_2 - \text{Er}_2\text{O}_3$ can be a useful refractory mixture for diode use.

In investigating the various systems Er_2O_3 , Y_2O_3 , and Ho_2O_3 with ThO_2 , the attractive properties of the rare earths are their low thermal expansion and good shock resistance. Thoria is attractive because of its inertness. Erbia is reactive and not very refractory. In order to achieve any substantially effective improvement by alloying with thoria, at least 50 mole percent thoria is believed to be needed. A 75-25 mole percent yttria-thoria mixture is scheduled for evaluation. An X-ray study is to be made of the systems $\text{ThO}_2 - \text{Y}_2\text{O}_3$ and $\text{ThO}_2 - \text{Ho}_2\text{O}_3$.

9.2 Thermal Expansion Effects

Important parameters in structural design of converters are the coefficients of thermal expansion of the construction materials and the effects of mis-match of these coefficients on the magnitude of the consequent thermal stress.

For solid solutions, an equation reported by Spurgeon¹ will yield a good approximation to thermal expansion, particularly when the solution involved is very near ideal.²

¹Spurgeon, W. M., Thermal Expansion Coefficient of Binary Substitutional Solid Solution Alloys, Thermodynamics & Transport Properties of Gases, Liquids, & Solids, ASME.

²For composite two-phase materials, thermal expansion can be predicted from Kerner's Equation

$$\alpha = \left[\frac{4G_o}{K_o} + 3 \right] \sum \left[\frac{\alpha_i v_i}{4G_o/K_o + 3} \right]$$

which is reported in Kirchner, et. al., Investigation of Theoretical and Practical Aspects of the Thermal Expansion of Ceramic Materials. Cornell Reports, P-1-1273-M-12 NOrd-18419.

$$\alpha_a = \frac{X_1 \alpha_1 V_1 + X_2 \alpha_2 V_2}{X_1 V_1 + X_2 V_2}$$

where: α = respective linear coefficient,
 X = mole fraction,
 V = atomic volume.

The probable cathode and insulator materials are shown in Table 9-1. The systems are either pure materials or solid solutions. The coefficients of thermal expansion for items 3, 4, 7 and 8 are those predicted from the relation cited.

Table 9-1 - Tentative Material Selection for Use at 2000°C

CATHODES		
Composition	Percent	Known or Predicted Expansion/°C
1. W	pure	4.6×10^{-6}
2. Re	pure	6.7×10^{-6}
3. W-Re	75-25	5.6×10^{-6}
4. Ru-Mo*	89-11	8.5×10^{-6}
INSULATORS		
5. ThO ₂	pure	10.4×10^{-6}
6. Y ₂ O ₃	pure	9.3×10^{-6}
7. ThO ₂ - Y ₂ O ₃	25-75	9.5×10^{-6}
8. ThO ₂ - Er ₂ O ₃	50-50	0.0×10^{-6}

* Cathode for 1500°C.

The alloy materials 3, 4, 7 and 8 in Table 9-1 will be fabricated and checked for thermal expansion by high temperature dilatometry to 2000°C (except for the ruthenium-molybdenum alloy which will be tested to 1500°C). This will provide data on expansion coefficients for design purposes and will help to uncover any spurious high temperature phase reactions.

9.3 Metal-Ceramic Stability

High temperature compatability tests between various ceramics and refractory metals, have been carried out at 1620°C in 0.1 micron vacuum (ion gauge) for 10 hours. Samples of mixed powders (-200 mesh) were blended together in the ratio 75 vol/percent metal 25 vol/percent oxide. The results of tests thus far are shown in Table 9-2.

Table 9-2 - High Temperature Reactivity of Ceramics and Metals

Decreasing Stability ↓		Decreasing Stability →			
		Tungsten	W-Yttria	W-Alumina	W-Erbia
	Columbium	Cb-Yttria	Cb-Alumina	Cb-Erbia	Cb-Holmnia
	Molybdenum	Mo-Yttria	Mo-Alumina	Mo-Erbia	Mo-Holmnia

Optical micrographs of the rare-earth, refractory-metals combinations show quite substantial intermediate phase formation present in the systems with higher reactivity. Molybdenum-holmnia are considered the most reactive. Electron micrographs and X-ray examinations of the above systems are planned. Another set of compatability tests is planned for 2200°C at high vacuum employing tungsten and rhenium in combination with thoria, yttria, and hafnia.

10.0 SEAL AND MATERIAL EVALUATION

10.1 Thermal Shock and Thermal Cycling Equipment

Few changes have been made in the thermal shock and cycling test equipment originally planned. None are of major importance. The equipment is currently in the process of being checked out.

A series of heating and cooling tests have been made using the state-of-the-art samples furnished by Red Bank and the equipment configuration shown in Figure 10-1.

The first group of tests in this series was run at three power levels, represented by plate currents of 0.5, 0.6, and 0.8 amperes, respectively. The resulting heating and cooling curves are shown in Figure 10-2, which was transcribed directly from the circular chart recording.¹ These were then differentiated to get the actual heating and cooling rates, as shown in Figure 10-3. Only the inner heat shield was used in this series.

The second group of tests were run at a constant power level, represented by $I_p = 0.5$ amp. The resulting curves, as above, are shown in Figure 10-4, and the differentiated curves in Figure 10-5.

Comparison of the cooling rate curves with similar ones derived from Skuta and Taulbee's analysis is made in Figure 10-6. As can be seen, the cooling rates are still too rapid for the purpose of this test. Additional shielding will be added as well as merely reducing the power input rather than shutting it off during cooling.

10.2 Cycling Control

Figure 10-7 shows our current thinking on an automatic cycling control. A timer has been built which will program the unit for a 90 minute repeating cycle with 32 minutes of "off" time. Use of the sapphire-

¹In the transcription process, the curves were shifted to a common origin in time in order to better display their relationships.

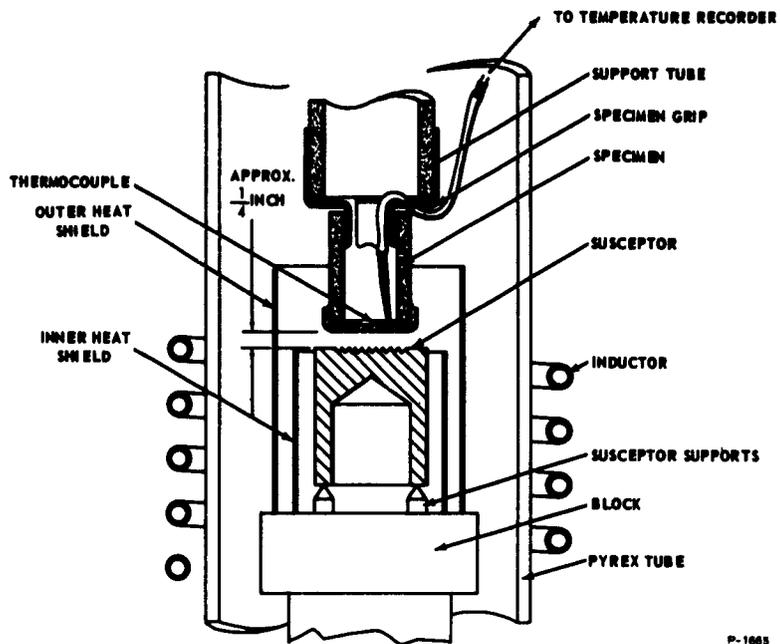


Figure 10-1 - Basic Test Arrangement for Heating-Cooling Tests

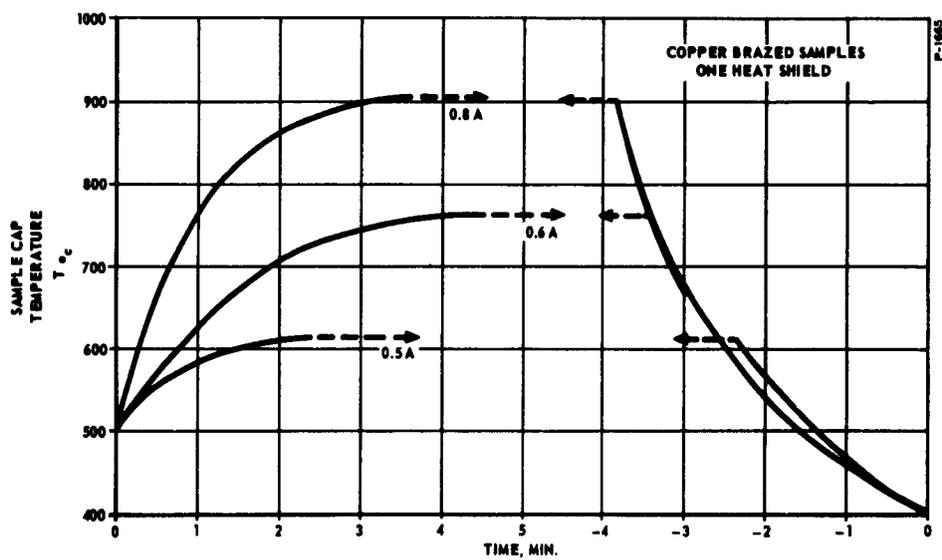


Figure 10-2 - Heating and Cooling Curves

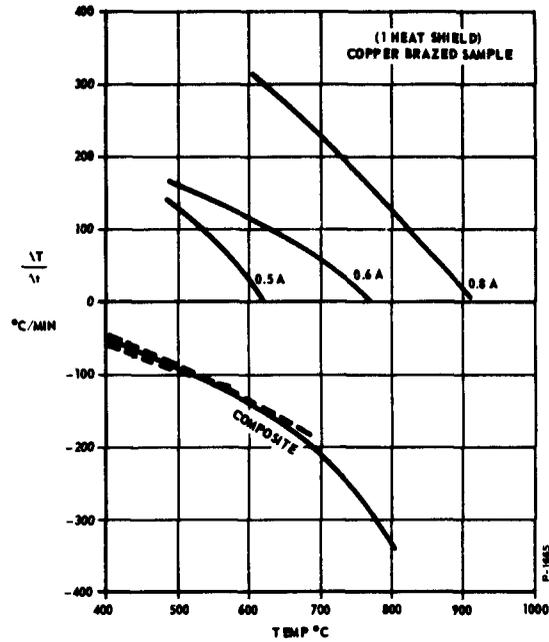


Figure 10-3 - Heating and Cooling Rates

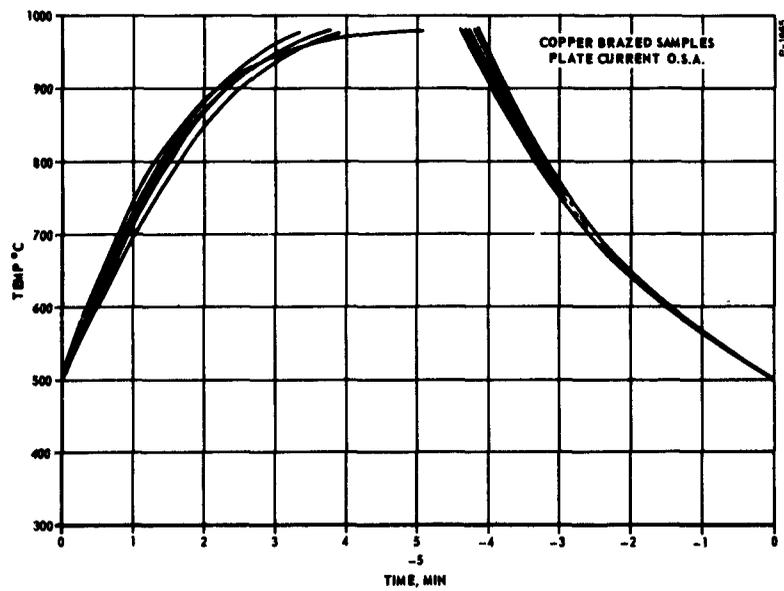


Figure 10-4 - Heating and Cooling Curves

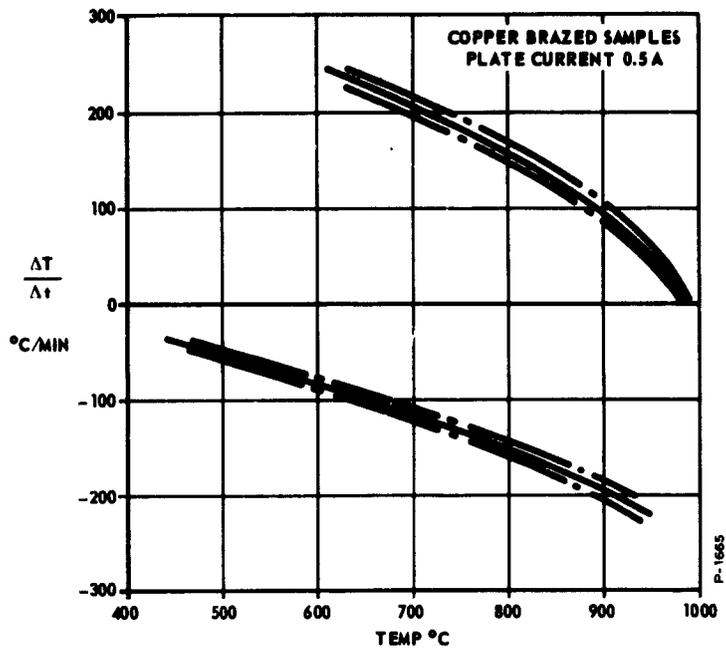


Figure 10-5 - Heating and Cooling Rates

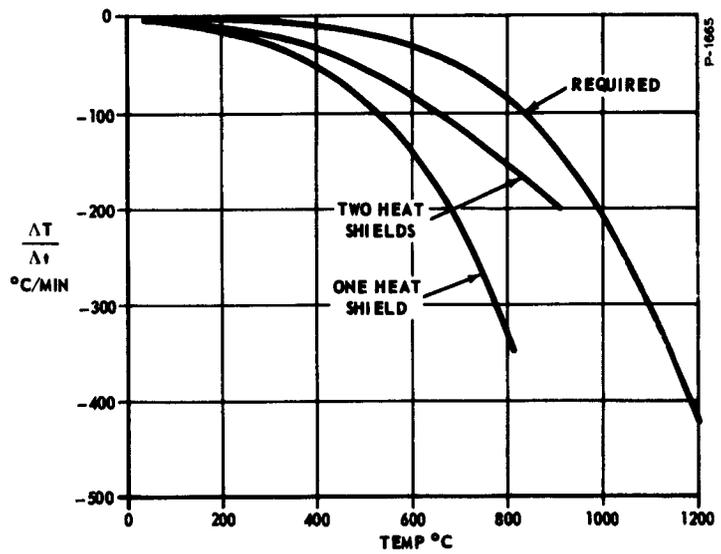
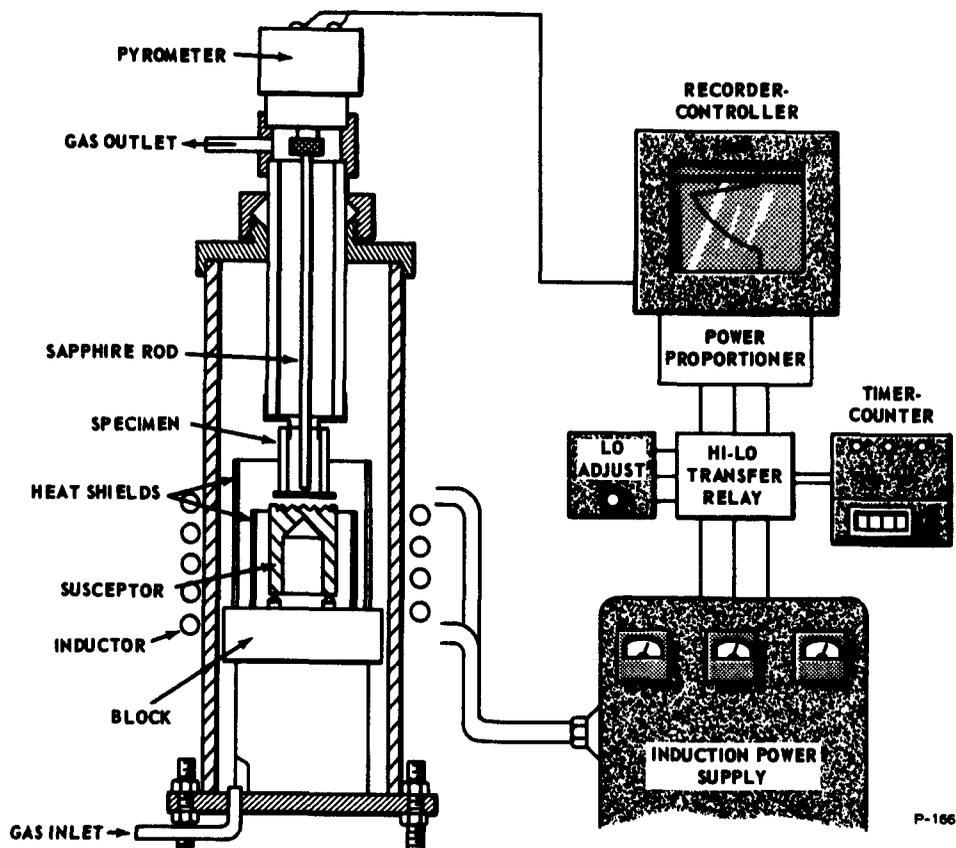


Figure 10-6 - Comparison of Cooling Rates



P-1665

Figure 10-7 - Proposed Automatic Cycling Control

rod pyrometer with the proportional-control unit now used for crystal pulling will allow holding at the upper temperature for the required time period. Cool-down rate will be controlled by adjusting heat losses with shields.

10.3 Cesium Compatibility

A literature survey was undertaken to compile the available data on the compatibility of the materials useful in this program with cesium. Using several abstracting services, and supplementing these with individual efforts, twenty (20) references of specific value have been identified. These are reported in Appendix A and are being studied for guidance in materials selection.

10.4 Plans for Next Quarter

Thermal Shock and cycle tests will be continued on the state-of-the-art specimens supplied by Red Bank. These will be cycled to 1050°C, approximately 30° below the melting point of the copper braze material. Different test equipment configurations will also be studied to determine if more suitable arrangements of susceptor and test sample are possible. Automatic cycling controls will be completed. Ceramic-to-metal seal specimens provided from the various tasks will be subjected to a standard test procedure for evaluation.

APPENDIX A
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