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CERAMIC TO METAL SEALS FOR
HIGH-TEMPERATURE THERMIONIC CONVERTERS

Third Quarterly Technical Report

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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 AF Aero-Propulsion Laboratory, Flight Vehicle Power Division (ASRPP-20). Mr. P. J. Hutchinson, (ASRPP-20/22208) is project engineer for the AF Aero-Propulsion Laboratory.

The report covers the work performed from 1 April 1963 through 30 June 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 third Quarterly Technical Report under Contract AF 33(657)-10038.

This report is unclassified.

ABSTRACT

This report covers work performed in the third 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 2000°C.

Work completed has enabled fabrication of alumina-molybdenum
structures which can resist a 1500°C environment. Ceramic-refractory
metal systems have been identified which are stable and usable up to
2000°C. Preliminary experiments to determine means of bonding these
materials for use at 2000°C have been successful. Elimination of
materials which are unstable when in the presence of cesium minimizes
possible corrosion effects. Recommendations are made for limitation
of the development activities to the most promising joint systems.

1.0   INTRODUCTION

The objective of this program is to develop ceramic to metal seals which are capable of long life at 1500 °C in cesium thermionic converters, and to extend the techniques developed and the knowledge gained to materials from which ceramic to metal seals can be formed capable of use at 2000 °C in cesium thermionic converters.

At the start of this program five potential methods of joining ceramic to metal for use at high temperatures were investigated. These potential methods are:

1. Use of high melting point brazing alloys.

2. The formation of an electroplated bond between metal and ceramic members.

3. Cold welding by ultrasonic methods.

4. Welding ceramic to metal by use of electron beam welding equipment.

5. The formation of a bond by the diffusion of compatible intermediate materials into both the metal and the ceramic.

The first three of these require that the ceramic have a suitably metallized surface. For this reason a study of metallizing materials was also undertaken.

A study of the feasibility of forming the emitter support and envelope wall structure from a single piece of composite material was also entered into. This structure was to be graded in composition from all metal at the emitter support end, to all ceramic at the other.

Study of the various joining methods was started utilizing alumina ceramics and molybdenum because these materials and information on them are readily available from commercial suppliers. At the same time, a study of the material properties of other ceramics and refractory metals was begun to determine the material systems which could be used at 2000 °C.

Conclusions drawn from the progress to date and recommendations based on these conclusions are contained in Sections 10.0 and 11.0.

2.0 METALLIZING PROCESS STUDIES

2.1 Work Completed

Becuase of the reported corrosive effects of cesium vapor on ceramic bodies which contain silica in any amount, ceramic formulations considered useful as the substrate for metallizing studies were limited to silica free aluminas. The following silica-free bodies are produced commercially and are readily available in shapes useful in thermionic converter structures:

99.5 alumina, 0.25 chromia, 0.25 magnesia
99.7 aluminia, 0.3 magnesia
98   alumina*
95   alumina*

In addition to these, the following two silica-free body formulations were found to be under development by ceramic producers:

98.0 alumina, 2.0 magnesia
alumina-magnesia spinel

Although sample pieces of these materials have been evaluated, neither body is available on a production basis.

The 99.5 alumina, 0.25 chromia, 0.25 magnesia bodies have been used to the greatest extent in the metallizing studies to enable rapid application of processes resulting from this work to commercially available ceramic pieces.

Tests of tensile strengths of the various metallizings reported previously were continued during the early part of this quarter using both flexure test techniques and ASTM standard procedures. Adhesion of metallizing to substrate was found to be poorer for all tested combinations of silica-free aluminas and metallizing slurries than for the same slurries on silica-bearing aluminas. This was, of course, expected from the reports of previous studies. Becuase metallizing adhesion was found to be generally improved by the addition of small amounts of titanium and/or titanium compounds and by increased sintering temperatures, the experimental activities were directed at evaluating the adhesion improvements which could be achieved by controlled variation of these processing variables.

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*Product of Silk City Ceramics and Tool Mfg., Inc., Hawthorne, N.J., exact formulation is held proprietary.

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In a paper reporting results of work at Los Almos Scientific Laboratory [1], it was noted that several fluxing constituents of refractory metal metallizing mixtures are unstable in contact with cesium. It was also found that an adherent coating of tungsten could be applied to a specially formulated, yttria-bearing, alumina body without the use of fluxes such as those required in conventional molybdenum-manganese metallizing processes.

The need for elimination of fluxing material in the metallizing was confirmed and use of conventional molybdenum-manganese metallizing slurries was discontinued. Attention was directed towards developing a metallizing method utilizing the capabilities of yttria to wet both alumina and tungsten or molybdenum.

Several high purity alumina bodies were metallized using tungsten-yttria and molybdenum-yttria slurries. Flexure tests of tungsten-yttria metallizing on 98 percent alumina, 2 percent magnesia bodies showed excellent adherence. ASTM tensile tests of this metallizing on 99.5 percent alumina, 0.25 percent chromia, 0.25 percent magnesia bodies gave extremely favorable results. Average strengths were more than two and one half times the tensile strength of the 99.5 alumina metallized with the moly-titanium system. Tensile strengths between 22,000 psi and 25,000 psi were obtained on individual test pairs. Ultimate failure occurred in the ceramic body, leaving the metallized surface intact.

2.2   Plans for Next Quarter

Additional ASTM test samples will be prepared using the tungsten-yttria metallizing system and varying such process controls as ratio of constituents and sintering temperature to optimize the processing.

A quantity of cylindrical test bodies of 99.5 alumina, 0.25 chromia, 0.25 magnesia will be metallized using the tungsten-yttria system. These will be used for high-temperature brazing studies.

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[1] R.E. Cowen, S.D. Stoddard, <u>Ceramic Materials for Nuclear Converters</u>, University of California, Los Alamos Scientific Laboratory., Los Alamos, N.M.; presented at American Ceramic Society Technical Meeting, 5/1/63.

3.0 BRAZING STUDIES

3.1 Work Completed

Brazed joints of the shapes shown in Figure 3-1 were formed between the metallized surface of 99.5 alumina, 0.25 chromia, 0.25 magnesia cylinders and both flat and cup-shaped molybdenum members. OFHC copper was used as the braze metal. In all test pieces made, the ceramic member was found to have cracked during processing. The cracks lay both in planes perpendicular to the cylinder axis, and in radial planes. They were located very close to the joint area.

The nature of the cracking, and some observations of the position of the metal members before and after processing have enabled some conclusions to be drawn as to the cause of the cracking. Figure 3-2 shows a sequence of drawings which illustrate the probable relationships (exaggerated for illustration purposes) of the cylinder and metal member during processing. As the temperature is increased, the greater expansion of the cylinder changes the relative location of originally adjacent surfaces of the cylinder and the metal part. When the braze metal is molten, and at the temperature of fusion of the braze metal, both members are unstressed. As the joint is cooled below the fusion temperature, the movement of members relative to each other which is necessary to restore the initial positioning is restrained by the braze. Internal stresses are developed in each member because of this restraint. The stress in the cylinder is tensile, one against which the ceramic in inherently weak, and results in failure of the piece.

The means of preventing such failures lies to a considerable extent in design to minimize stress or to cause unavoidable stresses to be of a nature which the parts best resist. Three methods are being tried to prevent ceramic failure; use of very thin metal members which will deform before ceramic failure; use of niobium in place of molybdenum to minimize differences in expansion coefficients; and change in the shape of the metal member to a straight sided cup instead of one with tapered sides. The ID of this cup will have to be matched very closely to the OD of the metallized surface of the cylinder. Because there can be no movement of a straight cup relative to the cylinder during processing, stresses in the ceramic which result from unequal expansion of the parts will be compressive.
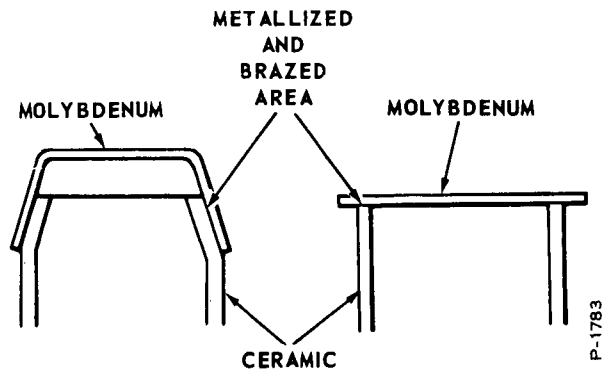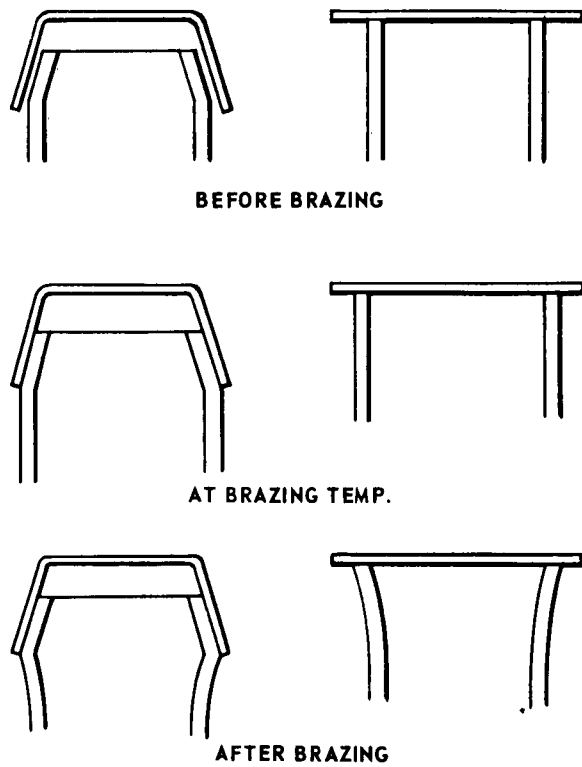
Figure 3-1 - Test Pieces for Brazing Trials

BEFORE BRAZING

AT BRAZING TEMP.

AFTER BRAZING

Figure 3-2 - Conditions of Brazed Joint Illustrating
Stress Development in Ceramic

3.2 Plans for Next Quarter

A number of ASTM test pieces and cylindrical test pieces which have been metallized with tungsten will be brazed to niobium and to molybdenum members. Braze materials will be iron, cobalt, and other braze materials which are expected to withstand a 1500°C environment. Testing will be performed to determine structural capabilities at high temperatures and whether seals remain hermetic after being stressed at high temperatures.

4.0 ELECTRON BEAM WELDING STUDIES

Although it was originally planned to carry on additional feasibility studies for welding of a metal member to the metallized surface of a ceramic body, equipment problems prevented this from being accomplished. No further activities are planned for this task. Preparation of a summary report has been started.

5.0 ULTRASONIC WELDING

5.1 Work Completed

Evaluation of the test samples from the second series of welding tests was completed. These tests were made on four groups of samples using Udimet 700 welding tips. Pertinent parameters for this series of welds are shown in Table 5-1.

Spot welds that showed good strength are shown in Figure 5-1. All welds were sectioned for metallographic examination. Figure 5-2 is a photomicrograph of a weld from Test Group 1. This shows one mil molybdenum bonded to the Mo-Mn metallized ceramic. It should be noted that there was an extremely large amount of turbulence of molybdenum metal at the interface. It is believed that this is the reason for a strong weld. In Figure 5-3 is shown a similar material system with welding parameters the same except for the weld time. In this instance it appears that another form of turbulence existed at the interface which caused a gathering of molybdenum metal prior to bonding.

When a tantalum interleaf is used as shown in Figure 5-4 a bond is made without distortion of the molybdenum. In this case, the tantalum appears to have doubled in thickness from the original 0.0005 inch at

Table 5-1 - Welding Parameters

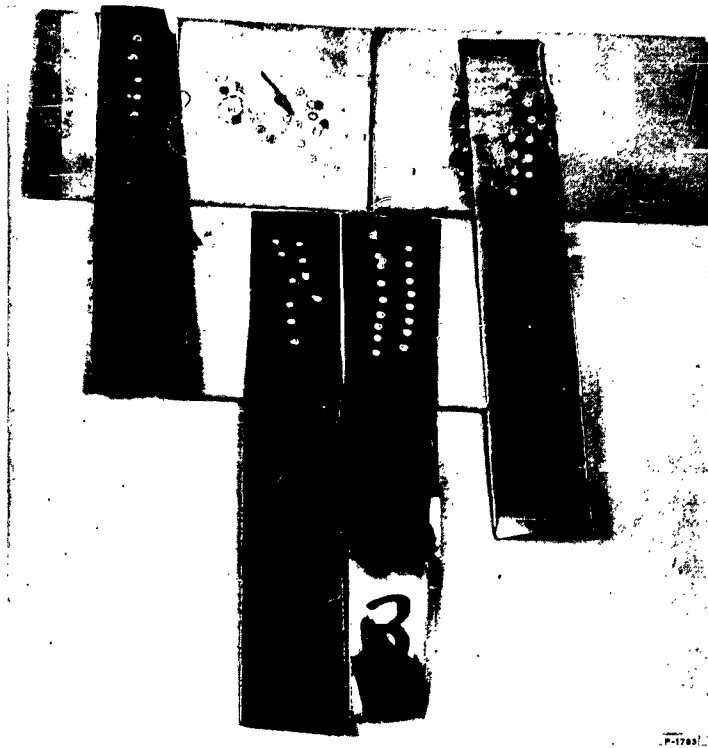| TEST GROUP	MATERIAL	POWER	CLAMP FORCE	WELD TIME	TIP RAD.
1	0.001" Mo to Mo-Mn coated Al_2O_3	6	20 lb Gage	1.0 Sec	2"
2	0.001" Mo to Mo-Mn coated Al_2O_3	6	20 lb Gage	0.1 Sec	2"
3	0.001" Mo to 0.0005" Ta to Mo-Mn coated Al_2O_3	5	25 lb Gage	0.3 Sec	2"
4	0.005" Mo to 0.0005" Ta to Mo-Mn coated Al_2O_3	5	25 lb Gage	0.3 Sec	2"

Figure 5-1 - Ultrasonic Welds of Molybdenum Sheet
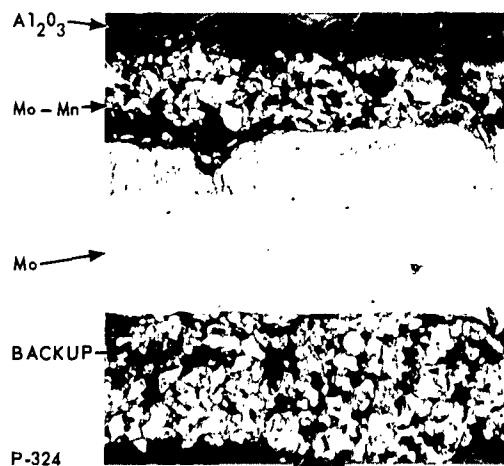to Metallized Alumina
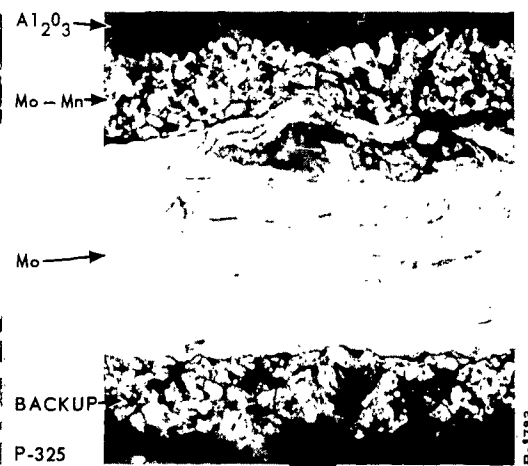

Figure 5-2 - Section of Group 1
Specimen

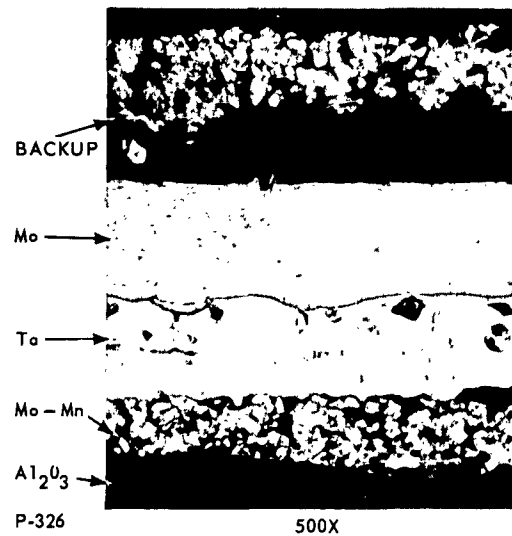Figure 5-3 - Section of Group 2
Specimen
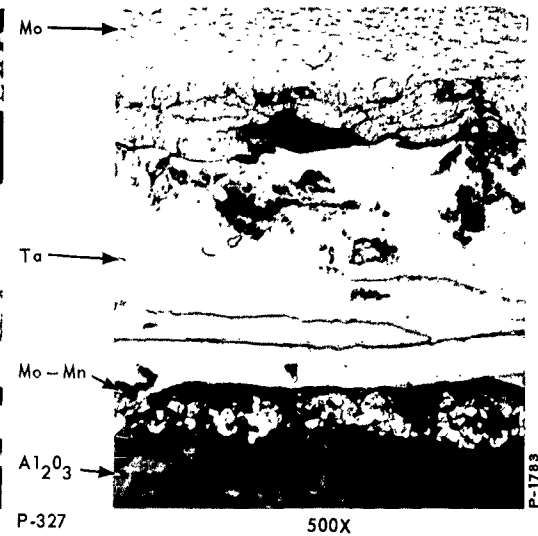
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Figure 5-4 - Section of Group 3
Specimen

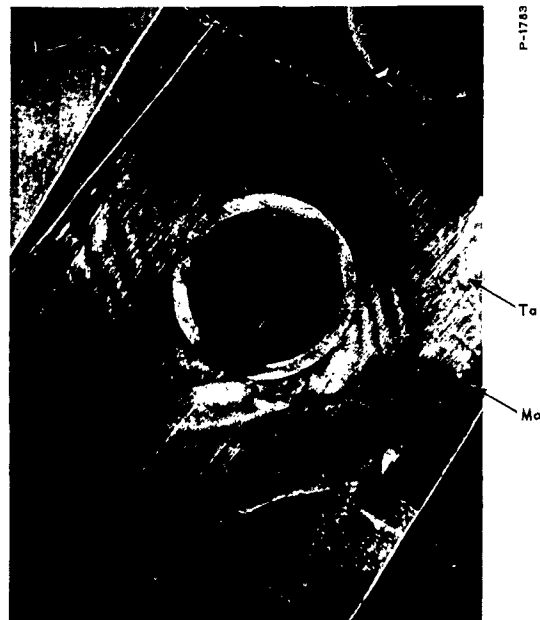Figure 5-5 - Section of Group 4
Specimen

Figure 5-6 - Tantalum Interleaf Used in Ring Welding Trials

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the weld zone. When 0.005-inch molybdenum was welded to the metallized alumina using a tantalum interleaf, a good bond was produced. In Figure 5-5 the section of such a bond shows interaction between the molybdenum and the tantalum, an extreme amount of gathering of tantalum metal, and a bond line between the tantalum and the metallized alumina that does not appear sound. The weld, however, was relatively strong.

Figure 5-6 shows the results of an attempt at ring welding molybdenum to a metallized alumina sheet using tantalum interleaf. The ceramic broke during the operation. The view in this figure is toward the side of the tantalum sheet which was in contact with the metallized surface. The unmarked section of the ring pattern could readily be due to ceramic breakage or to non-parallel faces. In ring welding the direction of tip motion is circumferential instead of linear. The direction of tip motion can be determined from this illustration by the stress pattern in the tantalum foil.

Results of the ultrasonic welding investigation indicate that many problems are yet to be resolved. Of these, the configuration, material, and surface finish of the welding tip are probably among the most important. An unanswered question is whether the alumina substrate would be able to withstand the ultrasonic energy imparted to it during welding without disintegration. An important consideration is the probable limit of metal thickness which can be used. It is limited to not more than 0.005 inch at the present time.

Activities in this task have been concluded.

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6.0   DIFFUSION SEAL STUDIES

6.1   Work Completed

6.1.1   Metal to Oxide Studies

Magnesium oxide-nickel interlayers were reported previously to be moderately successful in making an alumina-molybdenum seal after development of a spinel phase. However, difficulties were encountered in plasma spraying a uniform magnesium oxide layer, and marginal adhesion conditions resulted. Extremely high spraying temperatures were needed for the magnesium oxide and several water cooled nozzles were melted because of this. Small additions of other materials offered very little help in this respect; the magnesium oxide did not adhere and only a small amount would remain in the matrix of lower melting materials. Alumina dipped on a slurry of finely divided magnesium oxide again offered only moderate adhesion to the molybdenum. Only two samples were flame sprayed; SP-39 and 40. The nickel surface did not adhere to the plasma sprayed niobium and dipped magnesium oxide.

Because of these conditions, consideration was given to other possible interlayer materials. Niobium and niobium combinations were selected as among the most promising. It was necessary to evaluate a large number of possible coating combinations because of the possible large effect of small variations in material compositions. A complete list of the materials used in this phase of the study on the flat plates of alumina and molybdenum is shown in Table 6-1. Those material combinations which, in the flat plate study, showed most promise were applied to ceramic cylinders and metal caps for the formation of seals in this form. Table 6-2 is a list of the materials used on the molybdenum caps and alumina cylinders.

Better adhesion of the metallic interlayers was expected from a roughening of the surface of both the alumina and the molybdenum. Several methods were tested before the final choice was made; different grit-blasting air pressures were used on the alumina and the molybdenum, and plasma blasting was also employed with a small amount of alumina powder. The latter method provided a roughened surface but the particles deposited were only loosely attached and would not enhance mechanical adhesion. A very light grit blast -- about 10 psi with -60 mesh grit -- provided the best surface on the alumina pieces. The molybdenum required the same treatment to roughen the surface

Table 6-1 - Interlayer Materials Used on the Alumina and Molybdenum Flat Sheets

SAMPLE NUMBER	ALUMINA COATING	MOLYBDENUM COATING
SP-1	Ni	NiO
SP-2	Nb	Nb
SP-3	Ni	Ni
SP-4	50% Ni + 50% Al_2O_3	50% Ni + 50% Mo
SP-5	50% TiO_2 + 50% MgO	Ni
SP-6	50% Ni + 50% Al_2O_3*	Ni
SP-7	MgO	Ni
SP-8	50% MgO + 50% Al_2O_3	Ni
SP-9	MgO	NiO
SP-10	50% MgO + 50% Al_2O_3	NiO
SP-11	MgO	50% Ni + 50% Mo
SP-12	50% MgO + 50% Al_2O_3	50% Ni + 50% Mo
SP-13	Ni*	Ni
SP-14	Ni	50% Ni + 50% Mo
SP-15	NiO	50% Ni + 50% Mo
SP-16	50% Ni + 50% Al_2O_3	50% Ni + 50% Mo
SP-17	Ni	Ni Polished Surfaces
SP-18	--	
SP-19	Ni*	Ni Polished Surfaces
SP-20	--	
SP-21	Ni*	50% Ni + 50% Mo Polished Surfaces
SP-22	MgO	NiO
SP-23	50% MgO + 50% Al_2O_3	NiO
SP-24	Ni*	MgO
SP-25	Ni*	MgO
SP-26	Nb	Nb
SP-27	Nb	Nb
SP-28	80% MgO + 20% Ni	80% MgO + 20% Ni
SP-29	50% Nb + 25% Mo + 25% Ni	Same as alumina
SP-30	75% Nb + 15% Mo + 10% Ni	Same as alumina
SP-31	75% Nb + 15% Mo + 10% Ti	Same as alumina
SP-32	50% Nb + 25% Mo + 25% Ni	Same as alumina
SP-33	75% Nb + 15% Mo + 10% Ni	Same as alumina
SP-34	75% Nb + 15% Mo + 10% Ti	Same as alumina
SP-35	Dipped MgO Slurry	Ni
SP-36	Dipped MgO Slurry	50% Nb* 25% Ni + 25% Mo
SP-37	Nb	Nb
SP-38	Nb	Nb with Ni interlayer
SP-39	Nb	Ni (flame sprayed)
SP-40	MgO (dipped)	Ni (flame sprayed)

*Nickel coating was oxidized after being sprayed on alumina plate.

Table 6-2 - Coatings Applied to Alumina Cylinders and Molybdenum Caps
and the Resulting Pressures the Combination Withstood

SAMPLE NUMBER	ALUMINA COATING	MOLYBDENUM COATING	PRESSURE*
CY-1	Ni	50% Ni + 50% Mo	
CY-2	Ni	Ni	
CY-3	Nb	Nb	100μ
		Lapped Surfaces	
CY-4	Nb	50% Nb + 50% Mo	
		Lapped Surfaces	
CY-5	Ni (oxid.)	Nb	
CY-6	Nb	Nb	
CY-7	95% Nb + 5% Ni	95% Nb + 5% Ni	
CY-8	95% Nb + 5% Ti	95% Nb + 5% Ti	
CY-9	90% Nb + 10% Ni	90% Nb + 10% Ni	
CY-10	98% Nb + 2% Ti	98% Nb + 2% Ti	
CY-11	50% Nb + 25% Mo + 25% Ni	Same as alumina	
CY-12	75% Nb +15% Mo + 10% Ni	Same as alumina	
CY-13	75% Nb + 15% Mo * 10% Ti	Same as alumina	
CY-14	Nb	Nb	350μ
CY-15	95% Nb + 5% Ni	Same as alumina	115μ
CY-16	95% Nb + 5% Ti	Same as alumina	220μ
CY-17	75% Nb + 15% Mo + 10% Ni	Same as alumina	
CY-18	75% Nb + 15% Mo + 10% Ti	Same as alumina	
CY-19	Nb	Nb with Ni interlayer	120μ
CY-20	Nb	Nb	

*Minimum achievable on a Veeco Leak Detector. Only the samples that showed
any seal potential were tested on the leak tester; improper lapping and furnace
malfunctions caused the others to leak.

sufficiently. Great care had to be taken to avoid warping the thin
molybdenum sheets. This same technique was used on the alumina
cylinders and molybdenum caps. The irregular shapes caused some
concern that adequate uniformity of application might not be achieved.
Subsequent optical examination showed little variation.

All of the coatings used in this phase of the study were
applied with a thermal dynamics plasma flame F-40 torch unless other-
wise specified. Argon was found to be the best plasma gas for spraying,
but several materials were sprayed in nitrogen with relative ease. The
use of argon as the plasma gas reduced the possibility of contamination
and byproduct formation.

Since the coating is applied to a roughened surface, the resulting surface is also rough. In order to promote adhesion between the two roughened surfaces some of the samples were wet lapped, others were dry lapped, and still others were polished. More contact area could be afforded for the mating surfaces when they were lapped together. This is not as complete as polishing the surfaces, but it was sufficient to assist some material combinations in adherence.

Greater ease of application was experienced with the niobium separately and in combination with nickel, titanium, and molybdenum. Normally the samples were lapped or polished and placed in contact with each other under a pressure of 12-14 pounds per square inch. While in this configuration they were subjected to 3000°F for five hours in vacuum. The lapping operation is very critical on the cylindrical samples; great care must be taken in order to form a uniform circular surface that will provide the maximum area for diffusion to occur. This becomes a problem when more than one coating is applied to either surface because the cap becomes elevated as this thickness increases.

Several of the molybdenum caps were slightly out of round and this could have caused some of the leakage conditions noted in testing. The pressures recorded on the Veeco Leak Detector are listed in Table 3-2; only 5 of the seals were good enough to record a pressure. One hundred microns was the best pressure recorded, but two other cylinders held pressures near this value.

Figure 6-1 shows the contact area developed on the cylindrical samples when niobium alone is used; Figure 6-2 shows this same area when nickel is used with the niobium. The latter seal appears superior on both sample configurations. In general the niobium formed a very good seal with the roughened alumina, and there was little porosity in both the niobium and the niobium to niobium interface. A weak link occurred in the molybdenum-niobium interface where some voids appear (see Figure 6-3). The use of an interlayer of nickel which diffuses through the niobium appears to have some promise as shown in Figure 6-4.

The following conclusions have been drawn from the work done during the third quarter:

1. The magnesium oxide-nickel seal is too weak to provide a reliable leak-proof bond between the aluminum and molybdenum.
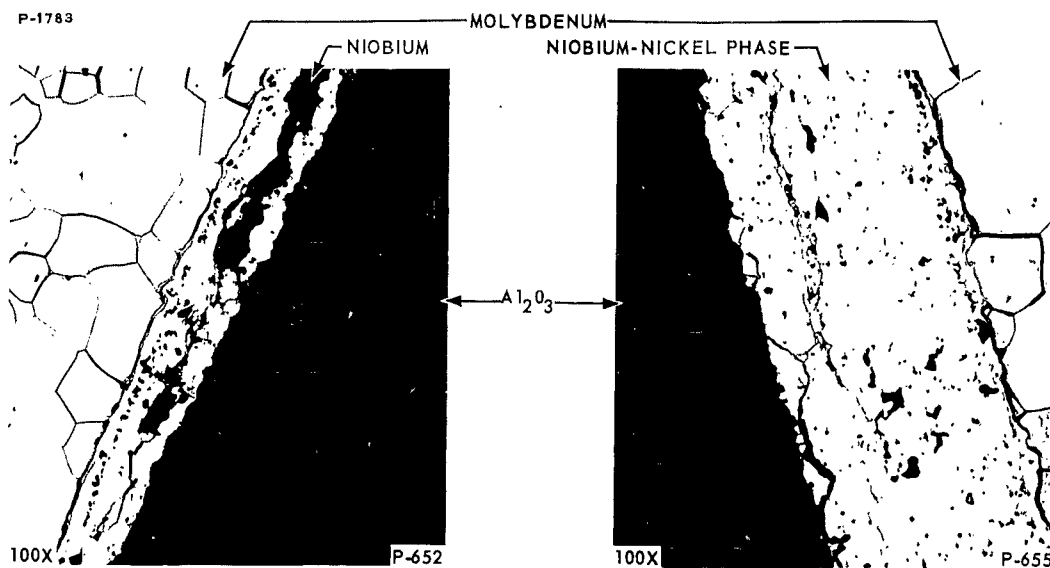
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Figure 6-1 - Molybdenum Cap and Al₂O₃ Cylinder with Plasma Sprayed Niobium Interlayer

Figure 6-2 - Molybdenum Cap and Al₂O₃ Cylinder with Plasma Sprayed Niobium and Nickel Interlayer
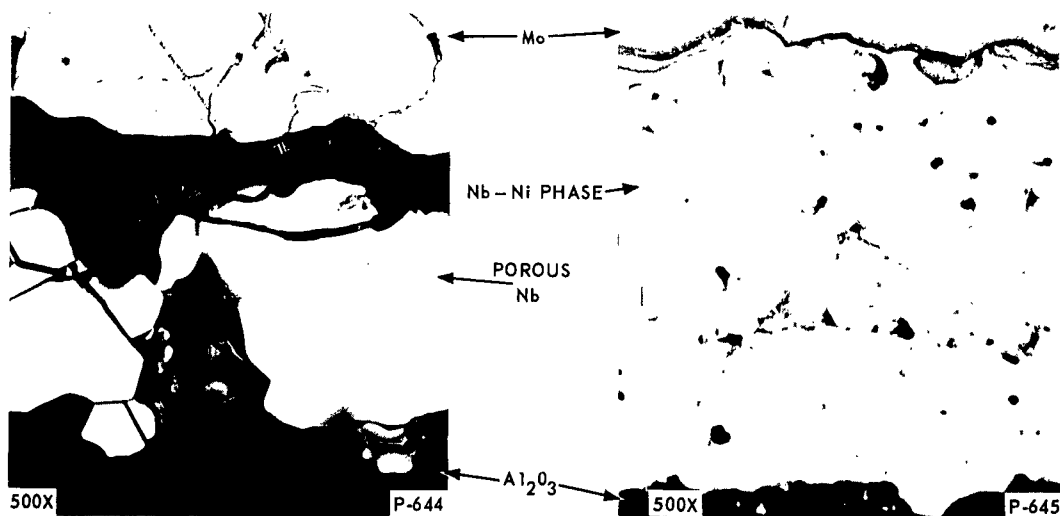
Figure 6-3 - Porosity in Seal between Molybdenum and Alumina Plates

Figure 6-4 - Molybdenum and Alumina Plates with Niobium and Nickel Interlayer

2. Light grit blasting of mating surfaces provided an improved working surface on the flat and cylindrical samples.

3. The plasma sprayed materials provided the most dense and adherent coatings.

4. Extreme care must be exercised when the surfaces are being lapped together; a greater contact area promotes a better seal.

5. Niobium base coatings have formed the best seals tested to date.

6.1.2 Metal to Metal Studies

Work was continued to find the optimum values for the many variables involved in making a strong diffusion seal of this type. Mechanically strong seals have been fabricated by diffusion sintering molybdenum sheet to alumina which was first metallized by a two-layer process. The first layer of metallizing uses an 85 Mo - 10 Mn - 5 TiH_2 slurry. The second metallized layer was composed of 80 Mo - 20 Cr. The chromium, being an actively diffusing metal, is used to promote sintering between the molybdenum sheet and the metallized layer. Total metallizing layer thickness is about 0.006 inch.

Surface preparation is an important variable in the processing of this bond. The molybdenum sheet was lapped flat and polished. The ends of the alumina cylinders were ground flat and parallel to within 0.0001 inch. After metallized, this material was lapped flat and polished. Final thickness of this layer is about 0.003 inch. The solid state diffusion by which a bond is formed was done at 1750°C - 1800°C for one hour.

Mechanically strong bonds have been obtained by this process, but due to the porosity of the metallized layer, the seals were not hermetic. A method was then devised to make the seal hermetic. In brazing with copper, the seals become hermetic because the molten copper filled the voids in the porous metal layer. However, in the solid state diffusion seal, the voids remain throughout the process. The method developed was to infiltrate the porous metallized layer with a compatible eutectic. The liquid phase would fill all the voids and transform the metallized layer into a non porous cermet. In essence, the seal would be a graded seal, metal to cermet to ceramic as shown in Figure 6-5.
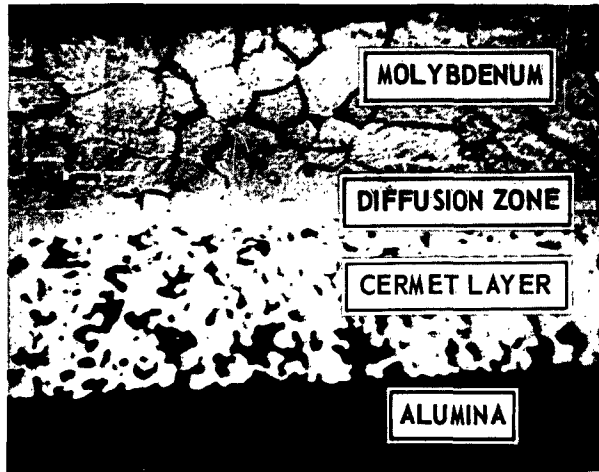
MOLYBDENUM

DIFFUSION ZONE

CERMET LAYER

ALUMINA

Figure 6-5 - Infiltrated Metal to Metallized-
Alumina Diffusion Bond

Four different methods of forming an infiltrated hermetic diffusion seal are being investigated:

1. After the alumina is metallized, a slurry of the eutectic mixture is painted over the metallized layer and fired at a temperature above the eutectic temperature. This melts, filling the voids in the metal layer. The infiltrated layer is lapped, polished and diffusion bonded to a molybdenum sheet.

2. After the solid state diffusion bond is made between a molybdenum piece and the metallized surface, the seal is infiltrated by painting the eutectic slurry at the joint. On firing, the liquid eutectic material flows into the voids of the porous metal.

3. The metallizing mixture can be applied to the molybdenum and fired instead of to the ceramic. The porous metal layer which is formed on the molybdenum can then be joined to the alumina by melting the eutectic between them.

4. The eutectic can be mixed with the molybdenum powder making a metallizing mixture which will form a non porous

metallizing coating when applied to the ceramic. The solid state diffusion bond would be made to the lapped and polished cermet layer.

Hermetic seals have been made by the first three of these methods. Attempts to form a seal by the fourth method have been unsuccessful to date. The most useful eutectic mixture used to date is one which melts at 1520°C. The infiltration steps are carried out at between 1600°C - 1650°C. If the infiltration is done at too high a temperature the eutectic will undermine the metallized coating and ruin the seal.

6.2   Work Planned for Next Quarter

6.2.1   Metal to Oxide Studies

Efforts will be centered on use of the niobium-nickel system as an interlayer sealant. A change will be made to niobium caps for the metal members. This is expected to eliminate the weak bonding area between the cap and the interlayer. Thermal expansion differences will also be minimized by this material change. Effects due to variation of the coating thickness and lapping will be studied to develop the best processing parameters for making reliable, vacuum-tight joints.

6.2.2   Metal to Metal Studies

Thermal cycling and tensile tests will be performed on a number of samples to determine the temperature and load limitations of seals formed by the methods described. All infiltration methods will be used in this study. Work will begin on developing solid state diffusion seals to the high temperature metallizings described in Section 2.0.

7.0 COMPOSITE ENVELOPE STUDIES

7.1 Work Completed

A primary objective of work done in this period was the fabrication of a continuously-graded, tungsten-to-alumina, vacuum-tight structure.

Considerable effort was expended in attempting to obtain continuously graded cups using the Sylco precision powder feeders, shown in Figure 7-1, and both die pressing and hydrostatic pressing techniques. Powder flow of alumina and tungsten can be controlled accurately with the Sylco machines. The principle limitation of this equipment is that the powders must be dry to prevent blocking of the powder flow.

Several attempts were made to circumvent this limitation, such as the use of activated alumina (alumina containing chemically combined
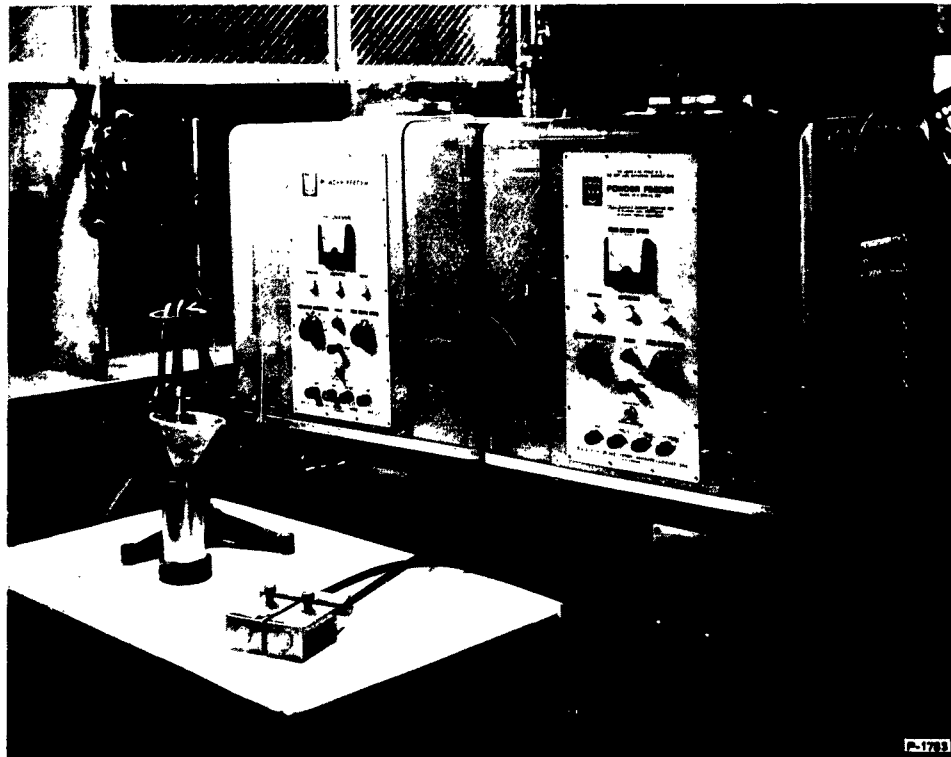

Figure 7-1 - Die Loading Equipment for Continuously Graded Composite

water), or the use of polyvinyl alcohol as an additive. In the case where activated alumina was used, a graded billet was successfully compacted by hydrostatic pressing at 40,000 psi. However, these billets could not be machined satisfactorily into a cup shape due to lack of strength in the unsintered condition. When polyvinyl alcohol was used the alumina material was first compacted using the chemical as a binder, and then was granulated to a size suitable for use in the powder feeders. This material could not be compacted at any reasonable pressure after granulation.

Another method tried was the addition of moisture in the form of 15 percent phosphoric acid solution after loading of the die. In all of these cases, which included over 30 billets, cracking occurred during drying due to nonuniform moisture distribution.

Simultaneously with the work on continuous gradation, the study of incremental gradation was continued. In the cup shown in Figure 8-1 of the Second Quarterly Technical Report, dated 15 April 1963, five increments were used:

AL_2O_3 %	Tungsten %
100	0
75	25
50	50
25	75
10	90

During the period now reported, a number of billets graded in 5, 6, and 7 increments were die pressed. Compacting pressure was varied from 20,000 psi to 40,000 psi, and drying temperature was varied from 140°F to 950°F. The results of these tests indicated that both pressing pressure and drying conditions are important processing variables which must be controlled within specified limits to produce satisfactory composite billets. Pressures of 30,000 psi were better than 20,000 or 40,000 psi and drying at 200°F appeared to be better than higher temperature drying. The use of magnesium stearate and 0.8% H_3PO_4 produced a billet that could be easily machined but still had considerable dry strength.

Figure 7-2 shows the composite envelope at three stages in the processing. The billet shown on the left has been die pressed at 30,000 psi, and dried at 200°F for 24 hours. The part shown in the center is
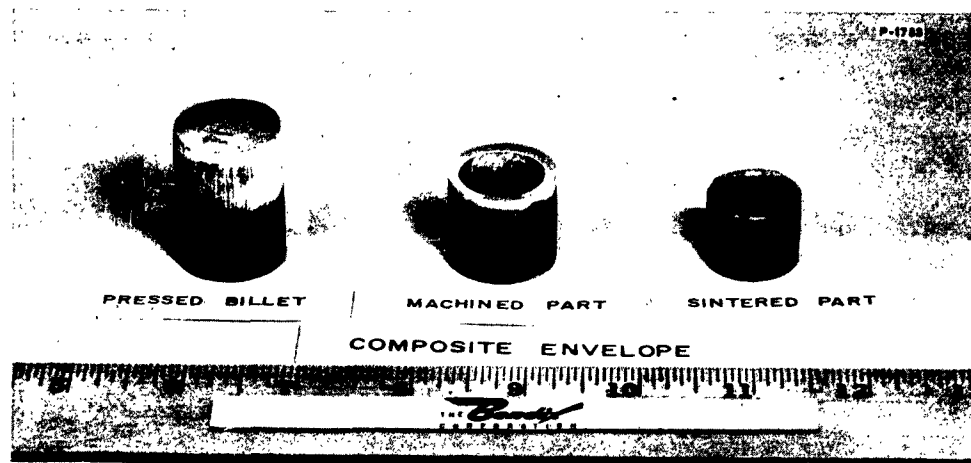
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PRESSED BILLET   MACHINED PART   SINTERED PART

COMPOSITE ENVELOPE

Figure 7-2 - Fabrication Stages of Composite Envelope

Table 7-1 - Composition of Laminations in Composite Cup

	ALUMINA* WT. PERCENT	TUNGSTEN** WT. PERCENT	PHOSPHORIC ACID*** WT. PERCENT
Closed End	5	95	0.40
	12	88	0.50
	23	77	0.50
	45	45	0.63
	64	36	0.75
	80	20	0.80
Open End	100	-	0.80

*Alumina: 73.5% A10 (-325)
              24.5% A5 (-100)
               2.0% Magnesium Stearate

**Tungsten: 99.75% M4O
               0.25 % Nickel (-325 Mesh)

***H_3PO_4 :   Reported as weight percent added as a 15% Aqueous
              solution to supply moisture for compacting

a similar structure that has been machined to form the cup-shape. On the right is a similar part after sintering at 3350°F for 1 hour. Details of the gradation used for these parts are shown in Table 7-1.

Several composite envelopes similar to that shown in Figure 7-2 have been sintered to date. None of these have been vacuum tight due to minor imperfections such as laminations, drying cracks, etc. The best of these maintained a 40 micron pressure. Another specimen which had an obvious pressing lamination maintained a pressure of 17 microns when the lamination was sealed with vacuum putty. This latter specimen has been subjected to one thermal shock cycle with no adverse effects.

The work carried out during this third quarter has led to the following conclusions:

1. Concept of a composite-shaped envelope graded from relatively pure refractory metal at the closed end to relatively pure ceramic at the open end appears feasible.

2. That this type of structure can be produced with alumina and tungsten has been demonstrated even though the expansion and sintering temperature differences of these materials are recognized as problem producing factors.

3. Pressing, drying, and sintering techniques are extremely important and will require considerable study to obtain a high degree of reliability in a production situation.

4. This type of structure should lend itself to other systems such as Al_2O_3-Nb, BeO-W, and HfO_2-Re.

7.2   Work Planned for Next Quarter

Work for the next quarter will be concentrated on the use of a greater number of increments and simultaneously reducing the thickness of each incremental layer in forming a billet. In this way, the characteristics of a continuously graded structure will be approximated more closely. The major portion of this effort will employ hydrostatic pressing since previous work has shown that this technique produces a more uniformly stressed compact of composite materials than does die pressing.

Development of techniques to produce continuous gradation will also be carried on. These will include efforts to add moisture while die loading is in progress to attempt to obtain better moisture distribution.

8.0 MATERIAL STUDIES

8.1 Work Completed

8.1.1 Oxide Systems

Small plates have been made from mixtures of thoria with erbia and yttria. The sinterability of the materials is excellent. X-ray examination of the samples indicates complete solid solution and excellent homogeneity. The lattice parameters of the thoria mixtures were calculated from the X-ray patterns and are plotted in Figure 8-1. The continuous line represents Vegard's approximation for lattice parameters of solid solutions. Accuracy of the calculated values suffers somewhat from line broadening, but the results illustrate a true solution behavior in changing from body centered cubic rare earth to cubic thoria. The length of the cube unit cell has been taken as $1/2$ a_o for the rare earths.

Hafnia has been stabilized with five and ten percent yttria. The stabilized hafnia appears to have excellent thermal shock resistance. For screening purposes, an oxy-acetylene burner was used to heat 3/8-inch diameter disks to 1700°C, followed by water quenching. Thoria samples cracked immediately upon application of heat. Yttria samples disintegrated on quenching. Stabilized hafnia remained intact but exhibited some microcracks.

Holmia has been dropped from consideration because of its chemical reactivity.

8.1.2 Metal-Ceramic Stability

High temperature tests of mixed powders have been performed in order to evaluate stability of proposed materials for 2000°C. Samples were held for one hour in vacuum of 10^{-5} Torr at the temperatures indicated in Table 8-1. Temperature was measured using both a total radiation and an optical pyrometer sighted through the hole in the lid on to the upper surface of the specimen lying in the bottom of the crucible. These two readings under approximate black body conditions were averaged.

The tungsten and rhenium combinations with yttria at 2300°C and 2365°C exhibited vaporization. Crystals on the crucible lids were examined by X-ray and found to be Y_2O_3. The rhenium-thoria
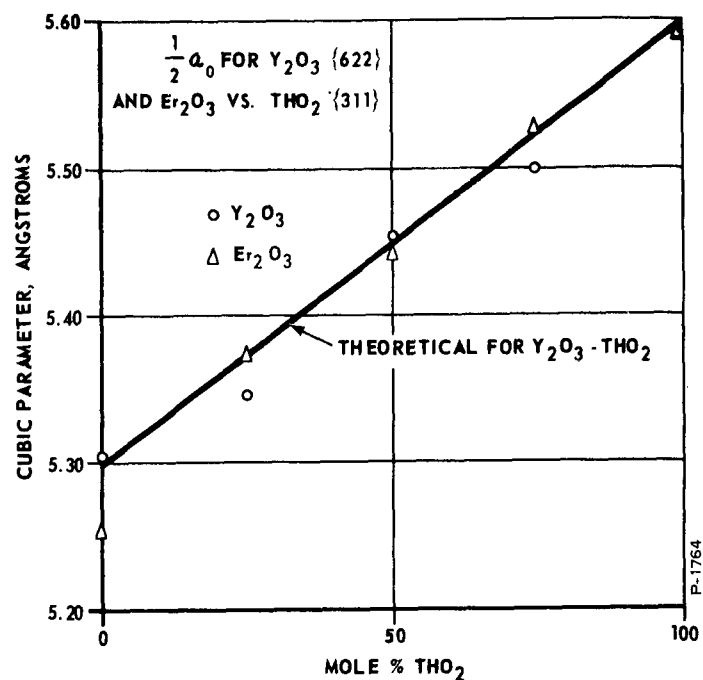
Figure 8-1 - Lattice Parameters for Cubic Solid Solutions of
Two Rare Earth Oxides in Thoria

Table 8-1 - Typical Values of Vacuum and Temperature
Metal-Ceramic Compatability Tests

COMPOSITION, VOL. PERCENT	TEMPERATURE	VACUUM (TORR)
75W 25 Y_2O_3	2300°C	2×10^{-5}
75W 25 ThO_2	2220°C	4×10^{-5}
75W 25 HfO_2	2290°C	2×10^{-5}
80 Re 20 Y_2O_3	2365°C	2×10^{-5}
80 Re 20 ThO_2	2445°C	1×10^{-5}
80 Re 20 HfO_2	2365°C	3×10^{-5}
80 Re 20 Y_2O_3	2045°C	2×10^{-5}

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sample heated to 2445°C also had crystalline material present on the crucible lid. This material was found to be crystalline ThO_2. The yttria mixture at 2045°C, the thoria at 2220°C, and both hafnia samples did not exhibit detectable vaporization.

The samples were examined metallographically. The rhenium samples were found to be extensively twinned under thermal stress. Optical micrographs at 500 diameters are shown in Figures 8-2 and 8-3. Figure 8-4 is a photomicrograph of tungsten and yttria after exposure at 2300°C.

An electron microscope was used to evaluate the results at higher resolution. Standard plastic negative replication was used to prepare microscope samples for examination. Oxygen solution in the rhenium and subsequent precipitation of oxide in twin lines was apparent. The effect is more severe at high temperatures as illustrated by comparison of the rhenium-yttria combination at 2045°C, shown in Figure 8-5, and at 2365°C, shown in Figure 8-6. Oxygen saturation of tungsten was not as apparent as can be seen in Figure 8-7.

Hafnia appears to be very stable in the presence of tungsten or rhenium, and for that reason is being considered as an insulator material. No interface reactions were noted with the exception that some transition zones were seen in the yttria mixtures; however, these would only be on the order of 2000 angstroms thick.

It is concluded that the principal systems W-Re, and ThO_2, Y_2O_3, HfO_2 should be excellent for use at 2000°C, at least as far as chemical stability is concerned.

8.1.3   Studies of Possible 2000°C Seal Systems

First attempts to braze 75 tungsten - 24 rhenium to yttrium oxide and hafnium oxide disks using yttrium as an active metal bonding agent were unsuccessful. Clean argon proved to be too oxidizing to permit melting, as did a vacuum of 10^{-4} Torr. The yttrium oxidized and powdered prior to melting, preventing any bonding. Some very slight amount of metal apparently remained when the melting temperature was reached in the vacuum trial and oxidized after melting. This was concluded since a melted reaction product was found on the hafnium oxide disk but had failed to wet the metal plate. This corrosion product was identified by X-ray examination as crystalline Y_2O_3.
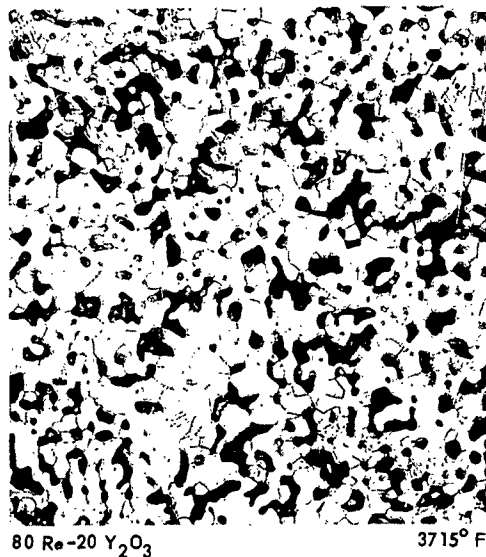
80 Re-20 Y$_2$O$_3$ 3715° F

Figure 8-2 - 500X Photomicrograph
of 80 Rhenium - 20 Yttria Mixture
Subjected to 2045 °C

80 Re-20 Y$_2$O$_3$ 4290° F
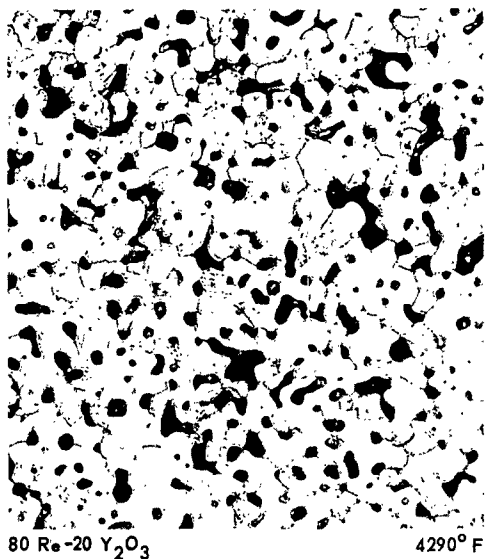
Figure 8-3 - 500X Photomicrograph
of 80 Rhenium - 20 Yttria Mixture
Subjected to 2365 °C

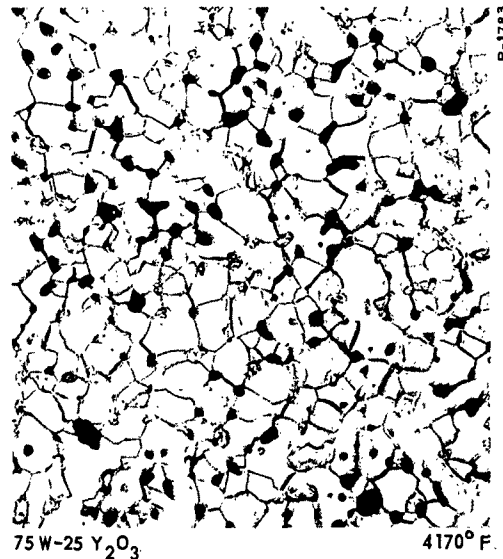75 W-25 Y$_2$O$_3$ 4170° F

Figure 8-4 - 500X Photomicrograph
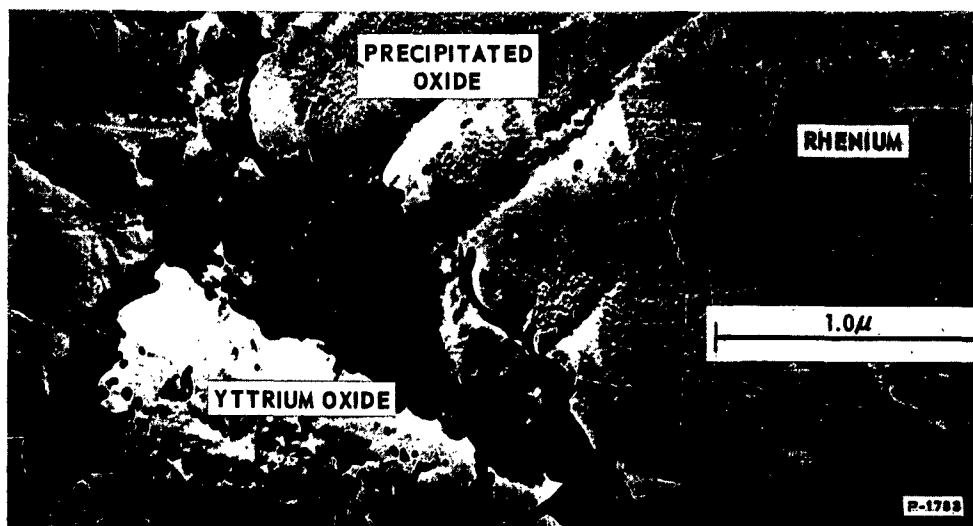of 75 Tungsten - 25 Yttria Mixture
Subjected to 2300 °C

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Figure 8-5 - 40000X Electronmicrograph of 80 Rhenium - 20 Yttria
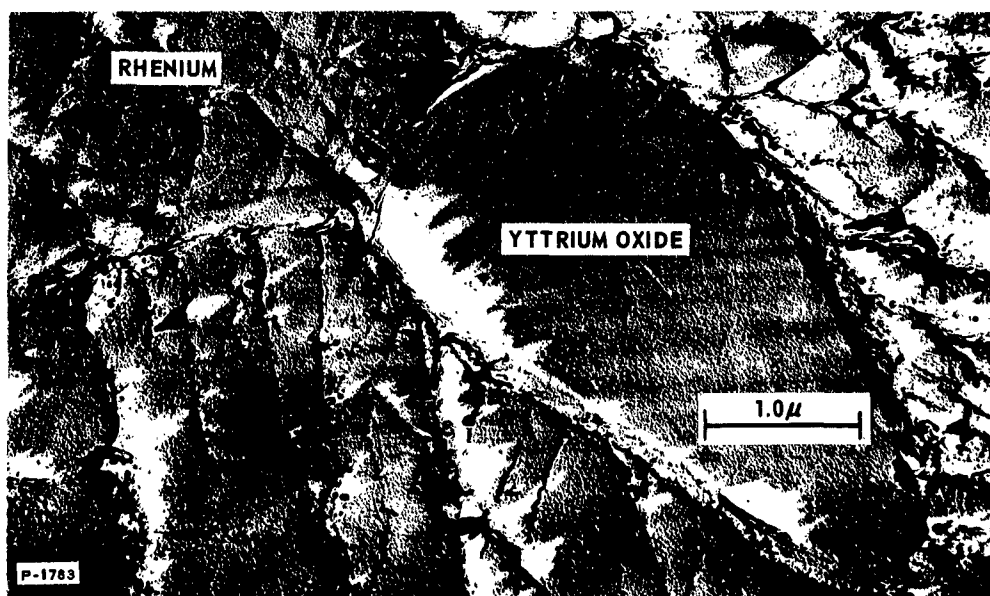Mixture Subjected to 2045°C

Figure 8-6 - 24000X Electronmicrograph of 80 Rhenium - 20 Yttria
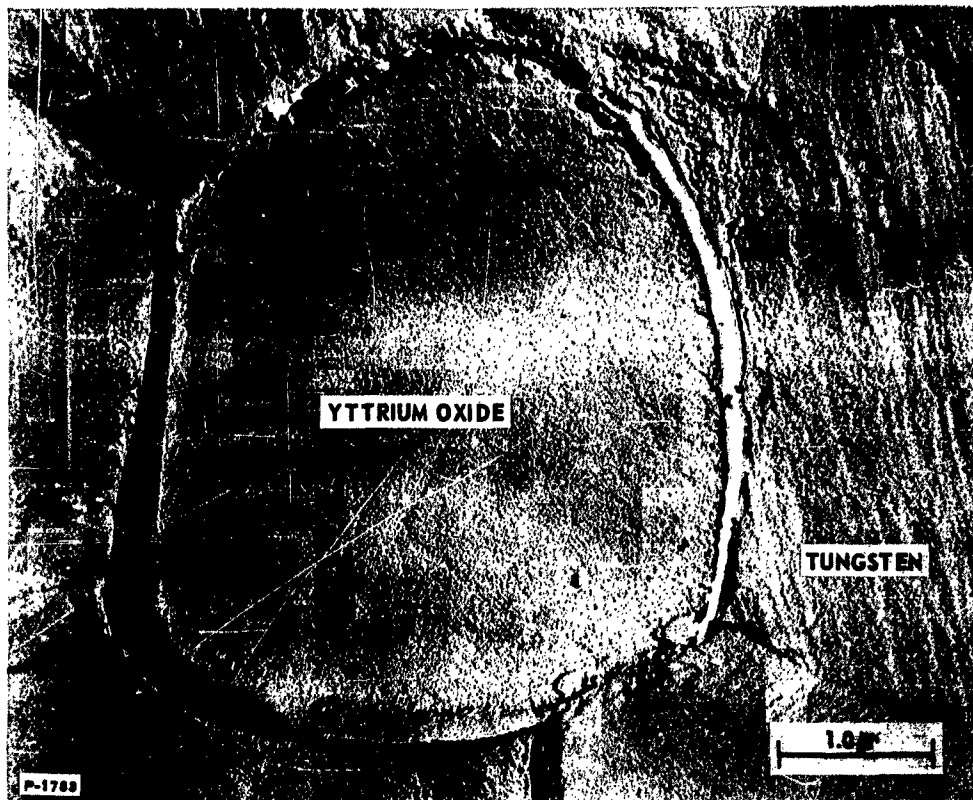Mixture Subjected to 2365°C

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Figure 8-7 - 24000X Electronmicrograph of 75 Tungsten - 25 Yttria
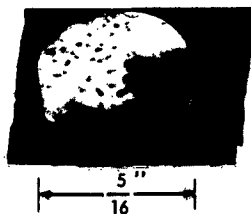Mixture Subjected to 2300 °C

Figure 8-8 - Rhenium-Yttria Sample Bonded
with Yttrium

A later experiment was successful. Figure 8-8 shows a yttrium oxide disk which was bonded to rhenium with yttrium. The bonding mechanism which occurred is similar to brazing. The bond was formed in a gettered argon atmosphere at 1600°C. The ceramic disk adhered tightly to the rhenium sheet. This sample was subjected to five thermal cycles between 500°C and 1400°C. The high temperature in this test was limited to 1400°C to remain about 200°C below the melting point of yttrium. The bond remained strong and the pieces intact.

The same sample was then subjected to 2000°C to determine the effects of exposing it to temperatures above the melting point of yttrium. The bond remained intact with no cracks or defects apparent in the pieces.

The two parts of this sample were then broken apart. Visual examination of the fracture area showed that a corrosion product had formed between the two members and that the break occurred in this corrosion product. It has been concluded that this corrosion product formed because of an excess of yttrium in the bond area. From metallurgical evaluation of the pieces, it was apparent that diffusion of yttrium had occurred into both the yttria and the rhenium, presumably during exposure to 2000°C. A true metallurgical bond was formed.

It is considered that reducing the amount of yttrium in the joint will improve the bond. It may also be possible to bond the yttria to the rhenium directly by the diffusion process. Such a bond should have properties which would make it usable at 2000°C.

Two subscale composite structures have been processed. These consist of a structure graded from pure rhenium to stabilized hafnia in one sample, and from 95 rhenium - 5 tungsten to pure yttria in the second sample. The tungsten addition was used in the second sample to enhance sinterability since sintering was not complete in the sample made with pure rhenium and hafnia. These samples were powder pressed and sintered in argon at 1800°C. The samples appear to be dense and sound under visual examination.

Figure 8-9 shows two views of the composite cup fabricated from pure rhenium powder graded into a 5 percent yttria -- 95 percent hafnia (stabilized) ceramic. Although gradiation was crude, and some difference in the sintering shrinkage of the materials was encountered, the cup was hermetic. The thermal expansions of rhenium and hafnia are closely enough matched so that even though gradiation was crude, it was adequate to achieve a sound body.

Figure 8-9 - Composite Cup Formed of Rhenium and
Stabilized Hafnia

This body has survived five thermal cycles between 500°C
and 2000°C. The cup appeared completed free of imperfections and
was hermetic after thermal cycling.

8.2 Work Planned for Next Quarter

Studies of active metal bonding with yttrium will continue.
Diffusion couples of tungsten and rhenium with yttrium metal interface
to yttria and hafnia will be investigated. Additional composite cups
utilizing the 2000°C material candidates will be fabricated and evaluated.

9.0 SEAL AND MATERIAL EVALUATION

9.1 Work Completed

9.1.1 Thermal Shock and Thermal Cycling Equipment

Evaluation of the induction-heated test arrangment showed that it would be impossible to provide the intended temperature profile for the thermal test cycle with existing equipment. Although sufficient power is available for heating the specimen, the control is too coarse for manual programming of the cooling rate, and the automatic control does not have the range to cover the full 500°C to 1500°C curve required.

Therefore, a resistance-heated furnace was built. This furnace consists of:

1. A water cooled base plate with feedthroughs for power, thermocouples, and argon

2. Water cooled terminals for attachment of the heater

3. A ceramic (zirconia) stool for the specimen

4. A series of heat shields

5. A water-cooled outer shell.

Power control for the furnace is provided by Leeds and Northrup recorder operated from W-5Re/W-25Re thermocouples in contact with the specimen.

9.1.2 Testing of Seal and Cup Samples

Three specimens have been subjected to thermal cycling tests in the resistance heated equipment. Two of these specimens were diffusion-bonded, infiltrated seals. The third was a graded composite cup.

The first diffusion bonded specimen was leak tested prior to cycling and found to be hermetic. It was then subjected to the heating and cooling cycle shown by temperature curve of Figure 9-1. This shows a heating rate of 500°C per minute up to about 1000°C and progressively less after that. As soon as 1500°C was reached, cooling was initiated. The rate of cooling was about 65°C per minute. After this cycle, the specimen was again leak tested and was found to be hermetic. Another cycle was then attempted using the temperature profile shown in Curve b

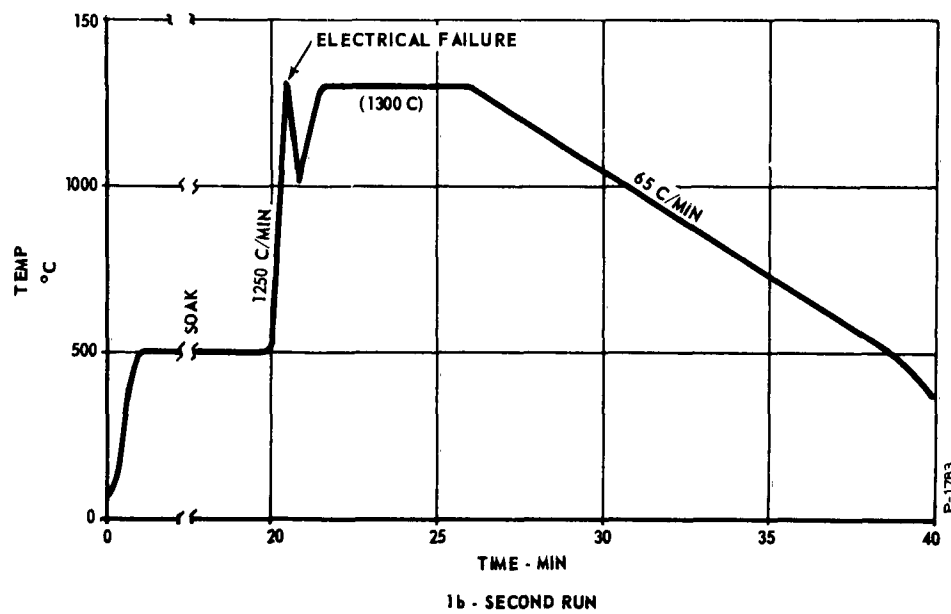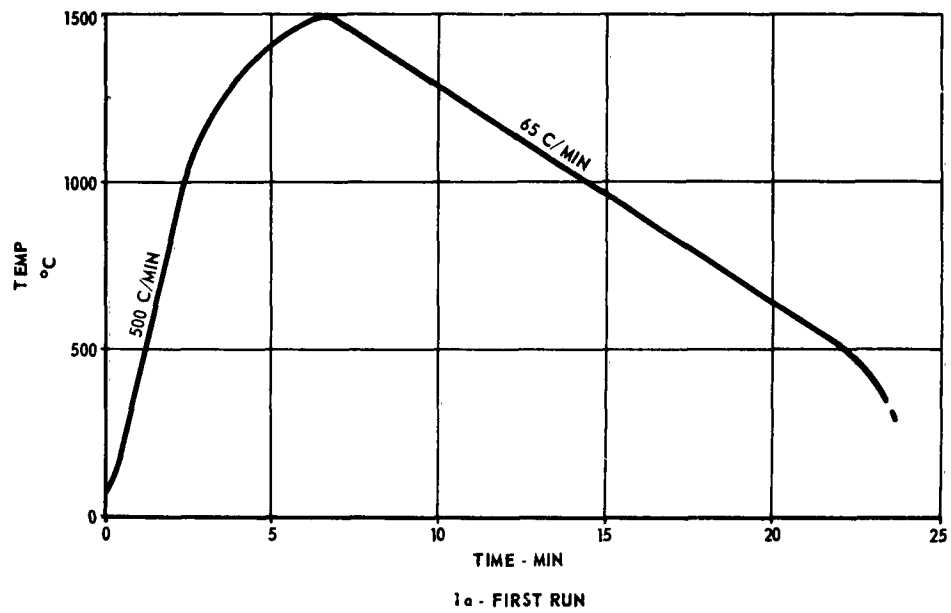1a - FIRST RUN

1b - SECOND RUN

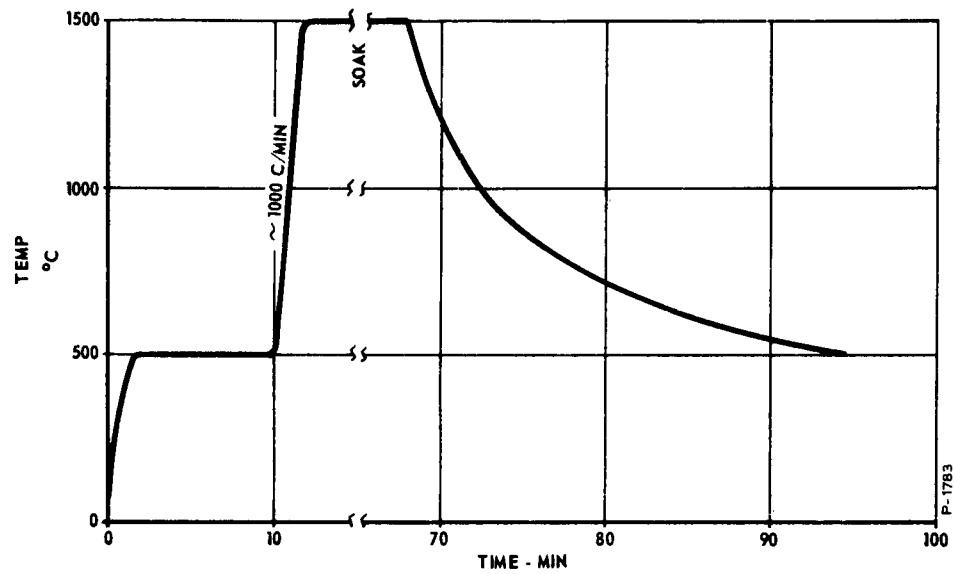Figure 9-1 - Thermal Cycle of First Diffusion Bonded Specimen

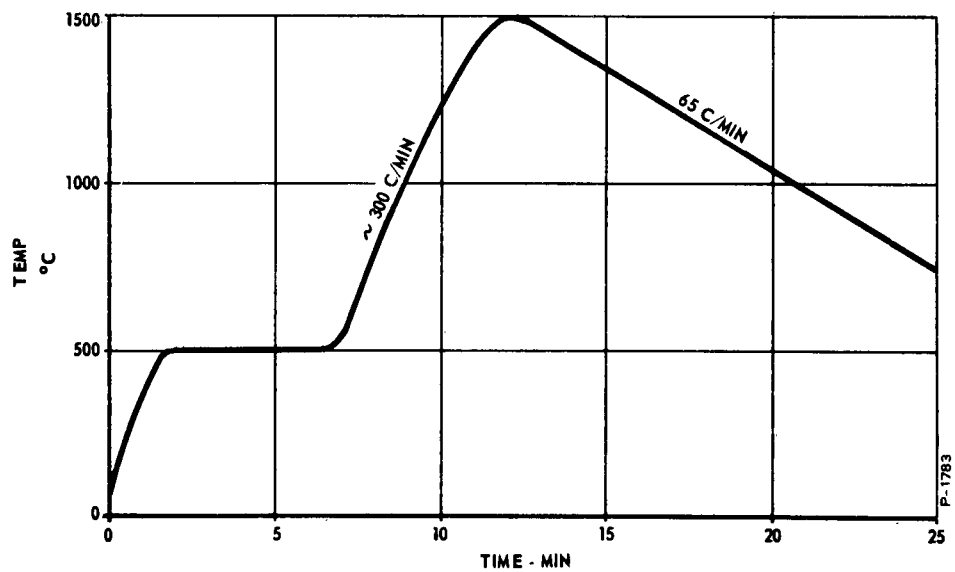Figure 9-2 - Thermal Cycle of Second Diffusion Bonded Specimen

Figure 9-3 - Thermal Cycle of Graded Composite Cup

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of Figure 9-1. An initial soak was performed for 20 minutes at 500°C since this is the lowest temperature the diode is expected to experience in earth orbit service, according to the environmental analysis reported in the First Quarterly Report. The temperature was then raised rapidly, at about 1250°C per minute. An equipment malfunction occurred at about 1300°C, and the specimen cooled rapidly to 1010°C before the equipment could be reset. A short soak at 1300°C (four minutes) was followed by cooling at 65°C per minute as before. After this cycle, the specimen was found to be cracked in the ceramic, both axially and circumferentially. It is believed that this was caused by the large temperature gradients that were induced during the uncontrolled portion of the cycle.

Another diffusion bonded specimen was given one full test cycle simulating orbiting temperature conditions as developed by the earlier analysis. This temperature cycle is shown in Figure 9-2. After testing, this specimen was found to be leaky in the bond area. Some discoloration in the vicinity of the bond indicates that something in the bond diffused into the ceramic; possibly the infiltrant or some oxidized molybdenum. Since the original shiny surface of the Mo emitter was also discolored, it is suspected that there was some oxygen present in the test chamber. There was no mechanical failure, either in the ceramic or in the bond.

The graded composite cup was known to be slightly porous as received. Because of the greater mass of the emitter the initial heating rate of this sample was slower than that to which the others were subjected, about 300°C/minute. The temperature profile of this test cycle is shown in Figure 9-3. Since the specimen was porous to begin with, no evaluation of damage based on loss of hermeticity can be made; however, there was no visible physical changes due to the temperature cycle.

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10.0 CONCLUSIONS AND RECOMMENDATIONS

10.1 Summary

During the course of this program, it has been determined that, at the present state of the art of three of the joining processes under study, they are not practical for fullfilling this fabrication requirement. Bonds between ceramic and metal members have been achieved by all processes being studied. However, inability to achieve hermeticity in the joint, inadequate bond strength, or impractical processing requirements have been the reasons why studies have been concluded on the formation of an electroplated bond, cold welding by ultrasonic methods, and the use of electron-beam welding of ceramic to metal.

Considerable success has been achieved in other tasks of this program. A metallizing process has been developed by which a strongly adherent sintered tungsten film can be applied to commercially available high purity, silica-free alumina. No fluxing materials or active metals which are susceptible to attack by cesium are used in this process. Diffusion bonds of several types have been formed, some of which have been tested at 1500°C successfully; i.e., with neither structural failure nor loss of hermeticity resulting from the test. Methods of fabricating graded-composition emitter and envelope structures have been developed for a tungsten-alumina composite. Because of the wide difference between expansion characteristics of these two materials, problems encountered in fabricating bodies with them would be considerably reduced when other material combinations are used.

Material systems which are considered most useful for this purpose at 2000°C have been generally identified. Some work has been started with these systems to determine applicable bonding mechanisms.

A physical bond has been achieved between yttria and rhenium using yttrium as the intermediate active metal layer to form the bond structure. A small body of graded composition utilizing rhenium and hafnia has been formed which has successfully withstood repetitive thermal cycling to 2000°C.

10.2 Conclusions

10.2.1 Seals for Use at 1500°C

The two ceramic to metal sealing processes which are immediately applicable to joining molybdenum and commercially

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available high-purity alumina for use at 1500°C are high-temperature brazing, and diffusion joining of molybdenum or niobium and alumina. Use of these joining processes is possible because of the development of a non-fluxed method of metallizing high-purity alumina with molybdenum or tungsten. Because all materials used in making these joints have been selected with a consideration of the need to resist a cesium environment, attack by cesium will be negligible.

Techniques have been developed for fabricating graded-composition ceramic-metal bodies in a form and size useful for emitter and envelope wall structures of thermionic converters. These techniques have been developed for the materials combination tungsten-alumina.

10.2.2 Materials and Seals for Use at 2000°C

Tungsten and rhenium, and hafnia, thoria, and yttria are the most promising refractory metals and ceramics for 2000°C service. The techniques developed for fabrication of composite bodies will be directly applicable to formation of composite structures utilizing these combinations of materials. The diffusion bonds, with and without intermediate active metals in the joint zone, which have been made with these materials, demonstrate high potential capability of providing the bond requirements at 2000°C.

10.3 Recommendations

10.3.1 Seals for Use at 1500°C

Although the activities which are planned for the next quarter can provide some basic data on the capabilities of the materials systems and the bonds developed, a test program of somewhat greater scope is required to demonstrate adequately the capabilities of these seals for the purpose intended. It is recommended that such a test program be undertaken, directed at defining in considerable detail the upper limit of temperatures which the diffusion seals and high temperature brazed seals can withstand reliably under the cesium vapor, vacuum, and thermal stress conditions of operational use. The effects of form and mass of the structural parts which make up the operational assembly are of importance in establishing bond capability. They should be duplicated in the test samples for the testing program to determine high temperature capabilities. The ultimate testing, therefore, would best be performed on high-temperature ceramic-metal structures built into operating converters of typical form.

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10.3.2 Seals for Use at 2000°C

Because of the success achieved in making the rhenium-hafnia composite, it is recommended that the development of a composite form for 2000°C service be undertaken using the rhenium-tungsten-hafnia-yttria family found to be most useful at this temperature. Studies of the effects of powder size distribution on density, body strength, and sinterability should be made. Process requirements to achieve sound hermetic graded cup forms in sizes usable for present converters would also need to be developed.

Since success was achieved in forming a bond between rhenium and yttria using yttrium as the active metal, it is recommended that studies of this bonding mechanism be continued on the 2000°C materials to better define the process requirements and the bond limitations. This investigation would be in the nature of a "back-up" to the program for the formation of a composite.

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