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HIGH TEMPERATURE CERAMIC-TO-METAL SEAL DEVELOPMENT

by

J. Chin and C. W. Messick

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ABSTRACT

This paper describes work to develop a ceramic-to-metal seal capable of operation up to 1200°C in a cesium environment. This development has been in progress since October 1965. A new metallizing technique, based on a promising tungsten-yttria system reported by Los Alamos Scientific Laboratory, was studied. Effects of mixture age, delay time between metallizing and brazing, and high temperature outgassing were measured and found critical to the final joint strength. Seals were prepared by brazing metallized Lucalox to niobium with a 60 vanadium - 40 niobium braze alloy. A complex braze thermal history was required for a high strength joint. A seal coat was developed which inhibits corrosive interaction between the braze alloy and alumina at high temperatures. With careful control of metallizing and brazing techniques, room temperature joint strengths equivalent to or better than early 700°C seals were obtained. Seals were subjected to thermal stability, and cesium corrosion proof tests and remained leak tight.

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INTRODUCTION

The objective of this program is to determine methods of producing ceramic-to-metal seals which will be stable in a cesiated thermionic diode for up to 10,000 hours at 1200°C. Commercial seals are not available which meet these requirements. Experimental seals were available at the start of this program which were designed for 700°C service. Litton Engineering Laboratories prepared this type of seal for early Gulf General Atomic thermionic test cells. A seal of this latter type, manufactured at GGA, has successfully operated in an out-of-pile test for over 17,000 hours in a cesiated environment at 700°C.

Metallized systems used for 700°C seal service contain SiO_2 and TiH_2 , which can be detrimental to the 1200°C seal concept. SiO_2 is susceptible to cesium corrosion and titanium reacts with Al_2O_3 . An improved metallizing system was required to meet program objectives. Copper-nickel braze alloys used for 700°C seals are obviously inadequate for 1200°C service.

A promising seal investigated here is the vanadium-niobium brazed Lucalox-to-niobium seal. Braze temperatures needed for vanadium-niobium alloys are above 1850°C. This is near enough to the reported 2050°C liquidizing temperature of Al_2O_3 ⁽¹⁾, that temperature control is critical. Stability of the braze alloy in contact with Al_2O_3 at brazing temperatures is questionable.

Ceramic-to-metal seals under development in this program consist of metal skirts (niobium) which are brazed to a ceramic (alumina) ring, see Fig. 1. Braze melt wetting and adherence to the alumina are provided by an intermediate metallized layer on the alumina. The development of a

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Fig. 1--(U) Ceramic-to-metal seal

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high temperature brazed seal thus consists of the following steps:

1. Development of an adherent metallized coating for alumina.
2. Determining the short time compatibility of the metallized alumina with proposed braze alloys and approximate thermal stresses which occur during brazing.
3. Examining braze temperature time profiles to determine optimum conditions for stress free joint preparation.
4. Determining methods of minimizing thermal stresses and chemical instability resulting from high temperature brazing of metallized alumina.
5. Optimizing metallized layer thicknesses and seal coat deposition procedures.
6. Evaluating alumina surface cleaning treatments before metallizing.
7. Monitoring the effect of seal fabrication processes on the microhardness and interstitial pickup of carbon nitrogen and oxygen.

Upon completion of these process studies completed seals are subjected to tensile, thermal stability, thermal shock, and cesium corrosion tests.

DEVELOPMENT OF AN ADHERENT METALLIZED COATING FOR ALUMINA

Industrial and literature surveys were made to find a metallizing system suitable to the needs of the high temperature seal concept. A W-Y₂O₃ metallizing system reported by LASL⁽²⁾ appeared promising and was selected for study. In the GGA version of this system, a W-2% Y₂O₃ metallizing mixture was brush coated on alumina as shown in Fig. 1 and heated to 1800°C in wet hydrogen. The apparatus used for this process is shown in Fig. 2. After holding for 40 minutes at 1800°C the sample was cooled in dry hydrogen to room temperature. Details of the metallizing

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Fig. 2--(U) Brush application of W-2% Y_2O_3 metallizing mixture to a Lucalox (Al_2O_3) ceramic

Fig. 3--(U) Induction heated hydrogen furnace

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process were examined to maximize coating adherence and determine the usefulness of this alumina surface treatment to the high temperature brazing of ceramic-to-metal seals.

LASL reported an age sensitivity of mixtures used for W-Y₂O₃ metallizing where the strength of the final seal decreased with the age of the W-Y₂O₃ mix. They recommend a maximum mixing time of less than one day, with four hours ideal. Age sensitivity of the GGA version of a W-2% Y₂O₃ metallizing mixture was evaluated and found to be insensitive to air aging up to ten days. Metallizing mixture age sensitivity effects were determined by peel strength tests. Peel strengths were measured with the apparatus shown in Fig. 3 mounted in an Instron tensile tester set at a cross head travel of 0.5 in/min.

The effect of air aging of the hydrogen fired W-2% Y₂O₃ metallized layer on the peel strength of copper-nickel brazed Lucalox-to-niobium seals was also evaluated. The results in Fig. 4 show the limiting maximum average value of the peel strength occurred when the niobium failed instead of the joint. The results suggest that for maximum joint strength ceramic-to-metal seals metallized with W-2% Y₂O₃ should be brazed within seven days after metallizing. If allowances are made for mixture variations, one should braze within four days after metallizing. Partial recovery of original peel strengths could be obtained by hydrogen refiring specimens air aged up to 148 days.

Bond strength degradation is thought to be due to air oxidation and adsorption of contaminants on the tungsten surface. The tendency of tungsten to oxidize at room temperature is evident from the free energy of formation of WO₃(s) (ΔF_f , 298), which is -182.6 K Cal/mole.⁽³⁾

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Fig. 4--(U) Peel test used to evaluate ceramic-to-metal bond strength, showing the peel test fixture mounted in an Instron tensile testing apparatus

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COMPATIBILITY OF METALLIZED ALUMINA WITH PROPOSED BRAZES AND
THERMAL TREATMENTS DURING BRAZING

Wettability Studies

Wettability of Litalloy, copper, Palco and a 60 V-40 Nb braze alloy on W-2% Y_2O_3 metallized Lucalox were compared. Samples of braze alloys, ultrasonically cleaned in acetone were placed on W-2% Y_2O_3 metallized Lucalox surfaces and heated in vacuo to braze melting temperatures. Rates of heating and maximum temperatures were compared with ceramic wettability by the braze alloy. The results showed all the alloys easily wet the metallized surface except 60 V-40 Nb. Rate of heating was critical to this alloy. Slow heating caused evaporation of vanadium, a change in alloy composition, and a change in the braze melting point. A rate of heating of at least $8^\circ C/sec$ during the last $50^\circ C$ was required for total melting, good flow, and good wetting by vanadium-niobium. Vanadium-niobium brazing was selected for the high temperature seal because of its compatibility with other components of the system and its high melting point.

Outgassing Studies

The effect of elevated temperature outgassing of metallized Lucalox in vacuo was examined. The object of this work was to determine if degradation of the metallized layer-Lucalox bond occurs during the V-Nb braze process. Metallized Lucalox specimens were heated in vacuo from $1500^\circ C$ to $1900^\circ C$ then cooled to room temperature. Peel specimens were prepared by brazing the outgassed metallized Lucalox rings to niobium skirts with a copper nickel alloy. Outgassing tests results were:

1. Metallized Lucalox specimens outgassed for two minutes at 1500, 1700, and $1900^\circ C$ showed no significant decreases in peel strengths over untreated control specimens.
2. Specimens outgassed for two minutes at $1800^\circ C$ showed slight increases in peel strengths over untreated control specimens.

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3. Specimens outgassed longer than two minutes showed significant reductions in peel strengths over control specimens.

It is thought that under limited outgassing in vacuo at 1800 and 1900°C detrimental oxides on the W-2% Y_2O_3 metallized surface are removed. Peel strengths of specimens prepared from these specimens were higher than aged specimens. Under extended outgassing, decomposition of Al_2O_3 -W system into Al, O, AlO, Al_2O , WO, WO_2 , WO_3 and $Al_2O_3^{(4)}$ degrades the brazed joint and low peel strengths again result.

EXAMINATION OF BRAZING TIME-TEMPERATURE PROFILES

Braze cooling profiles of the high temperature seal (Fig. 5) were examined in a series of tests in an attempt to:

1. Improve the consistency of the joints strengths.
2. Reduce stresses in the seal due to mismatched thermal expansion of the material components.

The effect of braze cooling on the peel strength of vanadium-niobium brazed Lucalox-to-niobium is summarized in Fig. 4. The curves show that short time holding at temperature reduces seal peel strength. Continued holding at temperature improves peel strength. The time required for this recovery is dependent on the temperature.

The test behavior of specimens which were quick cooled to room temperature after braze melting followed a familiar pattern. Peel strengths of one side of the seal joints were 50% higher than on the other side. Failure loads were erratic and varied. This behavior was also true of specimens heated above the braze melting point. Specimens held for one hour at 1400°C after braze melting and before cooling to room temperature were better. Peel strengths of these specimens were more uniform and more predictable although not as high as quick cooled specimens.

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Fig. 5--(U) Effect of delay time between metallizing and brazing on the peel strength of copper-nickel brazed, W-2% Y_2O_3 metallized Lucalox-to-niobium seals

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Holding at temperature anneals out differential thermal expansion stresses. Considering the final 1200°C use temperature, the shape of the peel strength curves, and the detrimental temperature effects, holding the braze joint at 1400°C for one hour plus 1200°C for one hour was chosen as a standard portion of high temperature seal preparation. A time-temperature curve of a typical vanadium-niobium brazed seal is shown in Fig. 6.

DETERMINING METHODS OF MINIMIZING THERMAL STRESSES AND
CHEMICAL INSTABILITY RESULTING FROM HIGH TEMPERATURE BRAZING

A side effect in specimens held at 1800°C after brazing was the corrosive attack of the V-Nb braze on alumina. Figure 7 shows corrosion caused by droplets of V-Nb braze alloy on samples of Lucalox held up to 120 seconds at 1800°C. All specimens had seen a temperature of about 1850°C. Areas of the specimen with braze droplets on metallized tungsten did not show the same corrosion. The corrosive attack observed in these tests reinforces the view that braze contact with the alumina surface is detrimental to the joint strength.

Of particular concern is peel failure noted at the Lucalox-metallized tungsten layer interface. This failure is thought to be partly a result of chemical corrosion due to high temperature interaction of braze which has penetrated the metallizing and alumina and partly mechanical due to thermal expansion mismatch of seal material components. Efforts were made to determine the contribution of each of these to joint weakening.

Two methods of reducing thermal expansion mismatch problems tried were: (1) elimination of the tungsten wire wrapping used for niobium-Lucalox pressure application, and (2) addition of a nickel flash coat to reduce braze temperatures. Reduction of chemical mismatch was attempted by vapor depositing tungsten on the metallized Lucalox. The purpose of this layer was to seal the surface and inhibit penetration of the braze through the porous metallizing, thereby preventing corrosive interaction between the braze alloy and Lucalox. The results of peel tests and

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Fig. 6--(U) The effect of braze cooling on the peel strength of vanadium-niobium brazed Lucalox-to-niobium

Fig. 7--(U) Typical V-Nb braze time temperature history

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microprobe and metallographic examinations of the specimens used to evaluate chemical and thermal mismatch can be summarized as follows:

1. There are no discernible differences in the failures noted in specimens prepared with and without tungsten wire wrap as a means of maintaining intimate contact between the niobium and Lucalox seal components. In neither case were there failures attributable to thermal mismatch. Seals prepared without tungsten wire wrapping had some void volume in the braze joint and exhibited greater variations in braze thicknesses along the braze than tungsten wrapped specimens.
2. Peel strengths of specimens prepared with a vapor deposited tungsten layer averaged higher values than those without this layer. A microprobe traverse of the braze-metallized areas show the vanadium to be sharply separated from the alumina (Fig. 8). This can be compared to penetration noted when no seal coat is used (Fig. 9).
3. Repeated cycling of specimens through the braze schedule improved the leak tightness and also increased diffusion of the braze into the braze and metallized layers (Fig. 10).
4. Trace addition of nickel to the brazed joint did not significantly reduce the brazing temperature or improve the joint strength.
5. Tungsten-nickel-niobium joints were obtained without a V-Nb braze foil. The peel failure of the resulting joint occurred primarily at the alumina-metallized tungsten interface. The peel strength of this joint was weaker than conventional V-Nb brazed joints. Nickel could not be detected by the microprobe in the joint after peel testing. Interdiffusion of tungsten and niobium occurred. This interdiffusion was not observed in specimens containing no nickel.

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Fig. 8--(U) Corrosive interaction between vanadium-niobium braze droplets held in contact with Lucalox at 1800°C for times shown

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Fig. 9--(U) Microprobe traverse of a V-Nb brazed, niobium-to-Lucalox seal with a tungsten barrier coat

Fig. 10--(U) Microprobe traverse before and after high temperature thermal stability testing

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METALLIZED LAYER THICKNESS AND SEAL COAT DEPOSITION STUDIES

It has been shown that a vapor deposited tungsten barrier coat reduces the diffusion of vanadium and niobium into the metallized tungsten layer. In early vanadium-niobium seal preparation a high percent of leaky specimens were made no matter how carefully the fabrication steps were handled. Leaky specimens were dye checked, peeled, then carefully examined by microscope and metallography. The examination showed unbonded areas and connected pores at the Lucalox metallized layer interface. Possible reasons for these problems are:

1. The sealed metallized tungsten layer was too thick and formed a rigid shell which separated from the alumina because of the differential thermal contraction of the alumina and metallized layer.
2. The seal coat was not uniform and did not permeate the metallized tungsten.
3. The Lucalox surfaces were not properly cleaned.
4. Niobium process treatments caused changes in the mechanical properties of the seal skirts.

Metallizing begins by mixing tungsten and yttria powders and amyl acetate with a small amount of organic binder. This slurry is then applied by brush to Lucalox. After air drying the ceramics are heated in wet hydrogen to 1800°C, held for 40 minutes then cooled in dry hydrogen. Control of coating thickness is dependent on the skill of the person applying it. One can, however, apply the coating qualitatively thin (4 - 14 μ) or thick (15 - 28V). Thicknesses of metallized layers including CVD-W seal coating were determined from photo micrographs and compared to peel strength and the percent of leak tight specimens (Fig. 11).

Peel strengths were found to be nearly independent of metallized layer thickness; seals prepared with thin coatings were slightly stronger

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Fig. 11--(U) Microprobe traverse of a vanadium-niobium brazed high temperature seal thermocycled three times to the braze temperature

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than thick coatings. This result is not considered significant since part of the high value peel strengths was caused by tearing of the metal tab during peeling.

Leak tightness of seal joints was found to be dependent on the metallized layer thickness. Thicker metallized layers produced a higher fraction of leaky specimens (Fig. 12). Only 17 percent of seals prepared without a seal layer were leak tight. Seals prepared with metallized layers thicker than 20 μ are only slightly better in leak tightness than seals without a sealed coat.

Seal coats were applied to metallized Lucalox ceramics at temperatures from 427°C to 650°C. The variation in peel strength of these specimens (Fig. 13) is not considered significant since part of the high averages were caused by metal tearing during specimen peel testing.

The dependence of specimen leak tightness on deposition temperature (Fig. 14) is thought to be the key to the success of the V-Nb brazed ceramic-to-metal seal. At low temperature the rate of tungsten deposition is slower which allows deep penetration of the metallized layer before pore bridging occurs. The effect of differences in deposition temperature can be seen in microprobe scans shown in Figures 15 and 16 and metallography, Fig. 17.

A summary of peel strength values for all seals regardless of seal deposition condition and metallized layer thickness are shown in Fig. 18. These are compared with room temperature peel strengths of copper-nickel brazed, niobium-Lucalox seals and V-Nb brazed seals without the seal coat or without the W-Y₂O₃ metallized layer. The results show that the room temperature strength of high temperature V-Nb brazed seal with a W-2Y₂O₃ metallized layer and a CVD-W seal layer are over twice the value of seals which have already been tested in out-of-pile tests for over 17,000 hours.

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Fig. 12--(U) Effect of metallized layer thickness on peel strength -Nb brazed ceramic-to-metal seals

Fig. 13--(U) Effect of metallized layer thickness on the percent of leak tight specimens

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Fig. 14--(U) Effect of seal coat deposition temperature on peel strengths of V-Nb brazed ceramic-to-metal seals

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Fig. 15--(U) Effect of seal coat deposition temperature on the percent of leak tight specimens

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NIOBIUM

VANADIUM

TUNGSTEN

ALUMINUM

Fig. 16--(U) Microprobe scan of a vanadium-niobium brazed seal with a 620°C, 20 second barrier coat (Specimen 3490-123)

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NIOBIUM

VANADIUM

TUNGSTEN

ALUMINUM

Fig. 17--(U) Microprobe scan of a vanadium-niobium brazed seal with a 427°C, 3 minute barrier coat (Specimen 3675-133)

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Fig. 18--(U) Optical micrographs of vanadium-niobium brazed ceramic-to-metal seals with barrier coats applied at (a) 620°C for 20 seconds and (b) 427°C for three minutes

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PREPARATION OF LUCALOX SURFACES FOR METALLIZING

A critical feature of all joints is the cleanliness of the interfaces to be joined. In ceramic-to-metal seals there are six interfaces--12 surfaces of concern. The braze alloy and niobium surfaces are cleaned by solvent degreasing, acid etching in nitric hydrofluoric acid and vacuum outgassing the niobium at 1400°C for one hour. The metallized layer surfaces are formed in situ and are thus considered clean.

Most of the effort given to cleaning preparations have been directed toward evaluations of cleaning treatments for the alumina.

Surface contamination which must be removed before good seals can be prepared include organics, metal chips, and ceramic grinding remanents. The alumina was first ultrasonically degreased in a mixture of solvents consisting of 35 methyl, ethyl ketone, 20 ethyl acetate, 15 toluene, 15 isopropyl alcohol, 10 acetone, 5 xylene (parts by volume). The remaining contamination is removed by burnishing in Al_2O_3 powder or etching in $HF-HNO_3$, or scrubbing with household cleanser, or air firing, or combinations of these treatments.

Trial cleaning treatment experiments are outlined in Fig. 19. The results show that the highest peel strengths were obtained in samples which included burnishing with alumina powder. Samples which had only been acid etched were not stronger than 36 lbs/in.

X-ray diffraction patterns of alumina surfaces which had been acid etched and those which had not were examined to determine if aluminum fluoride compounds formed on the alumina surface. Test results of this test were inconclusive. It is probable that fluoride compounds which might exist are below the detection limits for this technique.

Replica electron micrographs of Lucalox surfaces cleaned according to schedule, shown in Fig. 20, were prepared. Samples of the test results

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Fig. 19--(U) Ceramic-to-metal seal peel strength summary

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a = peel strength (lb/in)

Fig. 20--(U) Cleaning treatment and average peel strength of V-Nb braze Lucalox - niobium seals

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are shown in Figures 21-22. Where burnishing was used, sharp edges and surface cracks in the alumina surface were removed. Alumina powder remained on surfaces in spite of post water rinses.

Figure 21 shows that when acid etching is not accompanied by burnishing, the ceramic surface is clean but full of cracks. Peeling of metal to alumina seals could cause failure of these surface imperfections which would dictate an upper limit to the peel strength of these joints. The results of these experiments suggest that acid etching per se is not detrimental to surface cleanliness and can, in fact, aid clean up of residual materials.

A series of trials were made to determine the proper burnishing time. The results are shown in Fig. 23. Burnishing times the order of 30-40 hours are now being used for seal preparation for cells.

EVALUATION OF NIOBIUM USED IN SEAL FABRICATION

Important to the design of ceramic-to-metal seals is the reproducibility of material properties. Seybolt⁽⁵⁾ and Schofield⁽⁶⁾ have shown that the microhardness of niobium is a sensitive function of the oxygen content. Tottle⁽⁷⁾ has shown that the tensile strength is also a function of the oxygen content. What is true for the absorption of O_2 is also similarly true for the absorption of H_2 and N_2 .⁽⁸⁾ Thus a knowledge of the niobium microhardness after each stage of the fabrication is related to the gas contamination.

The results of niobium microhardness measurements are shown in Fig. 24. The results show that the microhardness of the final brazed niobium is not appreciably different than the original niobium sheet stock. These results were corroborated by results of trace gas evaluation (Table 1) which show that oxygen and carbon pickup during niobium processing are not significant. There were increases in the nitrogen contents of samples annealed in a resistance heated high vacuum furnace. The effects of these increases were barely detectable in the microhardness measurements.

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Fig. 21--(U) Cleaning schedule used for electron microscope
ceramic surface examination

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Fig. 22--(U) Replica electron micrograph of an alumina surface after Stripper cleaning, Ajax scrubbing, HF-HNO_3 etching, water and ether rinsing
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Fig. 23--(U) Replica electron micrograph of an alumina surface after Stripper cleaning, Ajax scrubbing, burnishing in Al_2O_3 powder and water rinsing
10,500X

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Fig. 24--(U) Effect of burnishing time on the peel strength of high temperature ceramic-to-metal seals

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TABLE 1
(U) ANALYSIS OF NIOBIUM AT SELECT PROCESS STEPS

~~(This table is classified Confidential Restricted Data Group 1)~~

	<u>N</u> <u>PPM</u>	<u>O</u> <u>PPM</u>	<u>C</u> <u>PPM</u>	<u>DPH</u> <u>Hardness</u>
<u>As Received</u>				
Litton Drawn	10, 11	191, 217	18, 19	100
GGA Drawn (Early)	71, 70	188, 188	16, 17	105
<u>Just Before</u> <u>Annealing</u>				
Litton Drawn	15, 27	81, 103	19, 21	
	46, 48	148, 160	27, 29	143, 147, 151, 133
GGA Drawn	23, 25	220, 226	32, 33	148
	13, 16	128, 151	20, 21	
<u>After Varian Furnace</u> <u>Annealing</u>				
GGA Drawn	76, 152	169, 183	23	96
	68, 84	169, 186	20	98
<u>After Induction</u> <u>Heated Annealing</u>				
Litton Drawn	26, 18	82, 82	21, 23	74, 76, 77, 87
GGA Drawn	10, 13	165, 185	29	91

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TENSILE TESTS

Peel strengths were used as a qualitative guide to bond strength. A special tensile test fixture with mechanical locking collars was built to insure that peel results were not giving false strength predictions for ceramic-to-metal seals (Fig. 25). The fixture and attached seals were mounted in an Instron tensile test machine. Tensile stress was plotted at a cross-head speed of 0.005 inches/min. Failure loads for Mark VIIB seals were 1140 and 2100 lbs. Cohesive failure of the alumina occurred. All ceramic-to-metal seal joints were intact (Fig. 26). These tests thus showed that the ceramic-to-metal joint was stronger in tension than the cohesive strength of the ceramic.

FLAT SEAL STUDY

Advanced thermionic reactor design analyses show that size and weight savings can be achieved if the current high temperature Litton geometry seal can be replaced by a flat seal. Two high temperature flat seal concepts are being examined to determine if replacement of the present seal configuration is feasible. One seal is a brazed flat seal. Experience gained in the development of the Litton geometry seal is applicable to the flat seal. Two jig fixtures have been used to braze high temperature flat seals. The first (Fig. 27) did not apply uniform pressure to the part and did not have the proper temperature response to produce good brazed joints. The second jig (Fig. 28) has been much easier to use, apparently applies a uniform load to the part and has an adequate temperature response. Fig. 29 shows a photomicrograph of the brazed flat seal cross section.

Graded flat seals prepared by GENMPO are also being evaluated. Preparation of these seals as reported by Gibson⁽⁵⁾ is by gas pressure bonding at 1650° - 1700° under a helium pressure of 10,000 psi. Pressure is maintained for six hours at temperature.

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Fig. 25--(U) Effects of process environments on the microhardness of niobium

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Fig. 26--(U) High temperature ceramic-to-metal seal in a tensile testing holding fixture

Fig. 27--(U) High temperature ceramic-to-metal seal after tensile testing

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Fig. 28--(U) Early high temperature flat ceramic-to-metal seal braze fixture

Fig. 29--(U) Recent high temperature flat ceramic-to-metal seal braze fixture

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Seals examined include:

- Type 1 Nb-graded layer- Al_2O_3 (Sintered)-graded layer-Nb (Fig. 30)
- Type 2 Nb-graded layer-Lucalox-graded layer-Nb (Fig. 31)
- Type 3 Nb-graded layer-alumina coated Nb-graded layer-Nb (Fig. 32)

Linde A Al_2O_3 with 0.5% MgO powder and niobium powder are used for graded layers. Concentrations of Al_2O_3 and niobium are gradually changed across graded layers to minimize interfacial stresses.

Microhardness examination of the niobium layers of test samples averaged 201 and 186 DPH respectively for Type 1 and Type 2 graded seals. Microhardness of annealed high purity niobium is typically 70-90 DPH. Contamination pickup is thus significant in these samples but much less than the Type 3 graded seal prepared with alumina coated niobium. The niobium layers in Type 3 samples average 377 DPH. Niobium grain size for these specimens ranged from 0.030 - 0.180 inches with large grains more numerous. Two Type 3 seals were electrically shorted.

Strength of flat brazed and graded seals have not been measured. Graded seals have been included in thermal stability and cesium corrosion tests. Flat brazed seals are a recent development and have not been available for stability tests.

THERMAL STABILITY TESTS

The long term 1200°C thermal stability test of three vanadium-niobium brazed niobium-to-Lucalox seals was terminated after a total of 2512 hours at temperature were accumulated. All seals were leak tight after the test and showed no evidence of gross change. The peel strengths of tested joints averaged 41 lbs/in. Microprobe traverses (Fig. 33) showed sharp boundaries between the tungsten and alumina layers with little evidence of braze component diffusion completely through the tungsten layer. Some interdiffusion between the tungsten and braze occurred.

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Fig. 30--(U) Photomicrograph of a V-Nb brazed flat seal
(200X)

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Fig. 31--(U) Photomicrographs at (a) 50X and (b) 200X of a Type I Graded Seal with a sintered powdered Al_2O_3 center and alumina-niobium graded zones

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Fig. 32--(U) Photomicrographs at (a) 50X and (b) 200X of a Type 2 Graded Seal with a Lucalox center and alumina-niobium graded zones

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Fig. 33--(U) Photomicrographs at (a) 50X and (b) 200X of a Type 3 Graded Seal with alumina coated niobium center and alumina plus alumina coated niobium graded areas

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Mark VIIA, Mark VIIB, a flat brazed seal and a graded flat seal were heated to 1400°C for 230 hours. An air leak terminated the test. Excessive oxygen pickup caused metal embrittlement which prevented peel strength tests. Grain growth in the metal skirts was obvious (Fig. 34). All ceramic-to-metal joints appeared intact.

Thermal shock resistance of a Mark VIIA seal heated 2512 hours at 1200°C was determined. The seal was found leak tight after 5, 15, and 50 thermal shocks between 200 and 1200°C. A heating rate of 1000°C per minute was used for these tests. Mark VIIA seal control specimens which were not heated for 2512 hours at 1200°C were likewise resistant to 50 thermal shocks. An early Mark VIIB seal thermal shocked 50 times between 300°C and 1200°C showed two cracks in the ceramic but no joint failure between the Lucalox and niobium. This led to additional annealing of Mark VIIB seals as previously noted. Recent Mark VIIB seals were thermal shocked 50 times between 300°C and 1200°C without failure. A flat vanadium-niobium brazed seal and a graded flat seal survived similar tests.

CESIUM CORROSION TESTS

A schematic diagram of the test apparatus used for cesium corrosion testing is shown in Fig. 35. Test specimens were sealed in a welded tantalum chamber fitted with a cesium reservoir. Specimen chamber temperature was made uniform through the use of guarded hot zones in a Pt-Rh Marshall tube furnace capable of 1400°C operation. Heat shields thermally isolated the cesium reservoir from the specimen chamber. Separate heaters were used to control the temperature of the cesium reservoir and its specimen chamber connection. Samples were outgassed to 1200°C at a pressure of 5×10^{-8} before the specimen chamber was pinched closed. Total time required for outgassing was 541 hours, this included 80 hours at 1200°C.

After outgassing the cesium reservoir was pinched open. X-ray examination of the cesium reservoir was made to insure cesium access to the specimen chamber.

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Fig. 34--(U) Microprobe traverses across a ceramic-to-metal seal joint
of a 2512 hour, 1200°C thermal stability test

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Fig. 35--(U) Mark VIIA ceramic-to-metal seal after
230 hours at 1400°C

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Ten ceramic-to-metal seals and one sheath insulator were corrosion tested. These included:

1. V-Nb brazed, Nb-Al₂O₃ seals with a barrier coated metallized tungsten layer.
2. V-Nb brazed, Nb-Al₂O₃ seals with a metallized tungsten layer.
3. V-Nb brazed, Nb-Y₂O₃ seals.
4. 60 Zr, 25V, 15 Nb brazed Nb-Y₂O₃ seals.*
5. 56 Zr, 28V, 16 Ti brazed Nb-Y₂O₃ seals.*
6. A GENMPO graded flat seal.**
7. A vapor deposited Nb-Al₂O₃-Nb sheath insulator.***

BeO-Nb seals were prepared but failed when outgassed.

Test specimens were heated to 1200°C and exposed to cesium from a liquid metal reservoir operating at 350°C. The test was terminated after 1950 hours at 1200°C. All specimens which were leak tight at the start of the test were still leak tight after the test.

The results of the visual examination of the specimens are summarized in Table 2. The general appearance of all specimens was good. There was no evidence of corrosion on the tantalum chamber walls. All weld joints appeared tight.

Samples from each test specimen were cut for metallography, microprobe, electron microscope and neutron activation analysis. Photomicrographs of cesium exposed V-Nb brazed Nb-Al₂O₃ high temperature seals could not be distinguished from control samples (Fig. 36). Large cracks were

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* Prepared by Eimac, San Carlos, California

** Prepared by GENMPO, Cincinnati, Ohio

*** Prepared by San Fernando Laboratories, San Fernando, California

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TABLE 2
(U) CESIUM CORROSION TEST VISUAL EXAMINATION SUMMARY

~~(This table is classified Confidential Restricted Data Group 1)~~

<u>Test Specimen Type</u>	<u>Appearance Change after Cesium Corrosion Testing</u>
V-Nb brazed, Nb-Al ₂ O ₃ Metallized Layer not Sealed	No attack in the joint, some blisters noted in unbrazed metallized areas.
V-Nb brazed, Nb-Al ₂ O ₃ Sealed Metallized Layer	No attack in the joint, some discoloration and lifting of the metallized layer in un- brazed areas.
Nb-Al ₂ O ₃ -Nb CVD Sheath Insulator	Pitting noticed at Nb-Nb interruptions.
V-Nb brazed Nb-Y ₂ O ₃	No Y ₂ O ₃ corrosion detected, gap between the braze and Y ₂ O ₃ ceramic.
60 Zr, 25V, 15 Nb brazed Nb-Y ₂ O ₃	Gaps between the braze and Y ₂ O ₃ ceramic noted, no corrosion of Y ₂ O ₃ detected.
56 Zr, 28V, 16 Ti brazed Nb-Y ₂ O ₃	Gaps between the braze and Y ₂ O ₃ ceramic noted, no corrosion of Y ₂ O ₃ detected.
Graded Seal	Grain growth but no corrosion on the niobium. Some gaps between the Nb and Al ₂ O ₃ noticed on the specimen O.D. No gaps noted on the specimen I.D.

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Fig. 36--(U) Schematic Diagram of the Cesium Corrosion Apparatus

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evident in all Y_2O_3 metal interfaces. The cracks appeared to have a mechanical origin rather than being the result of cesium corrosion. Cesium was not detected in any specimen joint with the microprobe. Interdiffusion of the vanadium-niobium layers occurred as expected but the ceramic-to-metal transition was sharp in all specimens. Figure 37 shows the results of a microprobe examination of one of the V-Nb brazed high temperature seals after 1950 hours at $1200^\circ C$ in a cesiated environment. Cesium pickup by test specimens was measured by neutron activation analysis. Cesium undergoes neutron capture according to the reaction $Cs_{133} (n, \gamma) Cs_{134}$. Cesium 134 beta decays to Ba_{134} with a 2.1 year half life. Beta detection was with a Ge Li detector. Tantalum interferes with this determination and must be chemically isolated. The results of this analysis are shown in Table 3. The differences in the accuracy of the measurements were due to differences in background interference. The results show nothing that would indicate cesium corrosion in any joints tested. Replica electron fracture graphs of peeled V-Nb brazed alumina niobium seals were prepared. Pitting seen in the alumina in Fig. 38 and not in the control specimen, Fig. 39, may be the result of cesium exposure. These pits were not observed on all specimens nor were they observed away from the exposed edge of the sample. The effect of these pits on the leak tightness and joint strength is not considered significant.

Microhardness measurements before and after cesium corrosion testing in the niobium and braze layers were the same as control specimens.

Peel strength measurements, Table 4, show all samples to be at least as strong as control specimens. Samples prepared with the yttria ceramics could not be fairly compared with the Nb- Al_2O_3 seals because of the poor performance of the yttria.

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Fig. 37--(U) Photomicrographs at 100X of V-Nb brazed seals
(a) exposed to a cesiated atmosphere for 1950
hours at 1200°C and (b) not exposed

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Fig. 38--(U) Microprobe traverse of a V-Nb brazed, niobium-to-Lucalox seal after 1950 hours at 1200°C in a cesium environment

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Fig. 39--(U) Replica electron fracture graph of an alumina surface near the edge of a peeled ceramic-to-metal seal exposed to cesium vapor for 1950 hours at 1200°C

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TABLE 3
(U) PHOTOACTIVATION ANALYSIS CESIUM CONCENTRATION IN SPECIMENS TESTED FOR
1950 HOURS AT 1200°C IN A CESIUM ATMOSPHERE

~~(This table is classified Confidential Restricted Data Group 1)~~

SPECIMEN NO.	CERAMIC	METALLIZED LAYER	BRAZE ALLOY	METAL SKIRT	CESIUM CONCENTRATION (PPM)	REMARKS
3479-47	Al ₂ O ₃	W-Y ₂ O ₃	60V - 40Nb	Nb	0.085	
3675-121	Al ₂ O ₃	W-Y ₂ O ₃ Sealed	60V - 40Nb	Nb	< 1	
3675-129	Al ₂ O ₃	W-Y ₂ O ₃ Sealed	60V - 40Nb	Nb	0.6	
3675-125	Al ₂ O ₃	W-Y ₂ O ₃ Sealed	60V - 40Nb	Nb	< 0.03	Untested control specimen
3479-109	Al ₂ O ₃			Nb	0.15	Graded Seal
3490-95	Y ₂ O ₃	W-Y ₂ O ₃	60V - 40Nb	Nb	1.4	
3479-139G	Y ₂ O ₃		56Zr, 28V, 16Ti	Nb	2.9	
3479-139K	Y ₂ O ₃		60Zr, 25V 15Nb	Nb	0.45	
3273-130	Al ₂ O ₃			Nb	< 0.8	Sheath Insulator CVD Nb and Al ₂ O ₃

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TABLE 4
(U) PEEL TEST RESULTS OF HIGH TEMPERATURE SEALS TESTED FOR 1950 HOURS
AT 1200°C IN A CESIUM ATMOSPHERE

... ~~(This table is classified Confidential Restricted Data Group 1)~~

SAMPLE	SKIRTS	CERAMIC	METALLIZED LAYER	BRAZE COMPOSITION	PEEL STRENGTH lbs/in	PEEL FAILURE *	REMARKS
3479-45	Nb	Al ₂ O ₃	W-Y ₂ O ₃	60V, 40Nb	15	A	Control, not Cs tested
3479-47	Nb	Al ₂ O ₃	W-Y ₂ O ₃	60V, 40Nb	39	A	
3675-121	Nb	Al ₂ O ₃	W-Y ₂ O ₃ + Barrier Coat	60V, 40Nb	122	A,C1	
3675-129	Nb	Al ₂ O ₃	W-Y ₂ O ₃ + Barrier Coat	60V, 40Nb	100	A	
367-133	Nb	Al ₂ O ₃	W-Y ₂ O ₃ + Barrier Coat	60V, 40Nb	75	A,C1	Control, not Cs tested
3479-139H	Nb	Y ₂ O ₃	Mo	56Zr, 28V, 16Ti	9	Am,Y	Control, not Cs tested
3479-139G	Nb	Y ₂ O ₃	Mo	56Zr, 28V, 16Ti		Y	
3479-139I	Nb	Y ₂ O ₃	Mo	60Zr, 25V, 15Nb	6	Am	Control, not Cs tested
3479-139K	Nb	Y ₂ O ₃	Mo	60Zr, 25V, 15Nb		Y	
3490-99	Nb	Y ₂ O ₃	W-Y ₂ O ₃	60V, 40Nb		Y	Control, not Cs tested
3490-95	Nb	Y ₂ O ₃	W-Y ₂ O ₃	60V, 40Nb		Y	Joint Strength approximately equal to con- trol specimen

- * A Adhesive failure between the metallized layer & Lucalox.
Am Adhesive failure between the braze and metallized layer.
C1 Cohesive failure of the Lucalox.
Y Yttria crumbled during peel testing.

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Fig. 40--(U) Replica electron fracture graph of an alumina surface of a peeled V-Nb ceramic-to-metal seal

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