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Metal-to-Ceramic Seals for Thermionic Converters
A Literature Survey

W. M. Phillips

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**JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA**

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Preface

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Abstract

The available unclassified literature in the field of metal-to-ceramic seals has been reviewed for the applicability of various sealing techniques to nuclear thermionics. Evolution of current techniques is presented, with some comments on possible techniques that could be explored further should alternate seal fabrication methods be required. Data on corrosion resistance of braze alloys in cesium and irradiation damage to ceramics is also presented. The techniques currently applied to thermionic diodes is also briefly outlined.

Metal-to-Ceramic Seals for Thermionic Converters: A Literature Survey

I. Introduction

This literature survey was undertaken to outline possible fabrication techniques for metal-to-ceramic seals applicable to in-pile thermionic converters. Surveys of seal technology have been periodically undertaken and are available in the literature, among which is a report of very wide scope published by the Air Force Materials Laboratory (Ref. 1). Less extensive surveys have been published in a variety of journals (Refs. 2-4). Since the publication of these reports, considerable additional data have become available on aspects of metal-to-ceramic seals of particular interest to the thermionics field, e.g., irradiation damage to ceramics, alkali metal corrosion, additional active metal brazing techniques, and improved, graded, cermet seals. This survey attempts to outline and summarize the later work as well as the earlier techniques that may be of interest in the thermionics field.

A. Evolution of Sealing Techniques

Initial documentation of metal-to-ceramic sealing technology is usually attributed to Pulfrich, Magner, and Vatter. Pulfrich's patents (Ref. 5) describe metallizing of ceramics by the painting of a layer of molybdenum, rhenium, or tungsten powder, in a binder, on to the surface of specially formulated steatite, followed by controlled atmosphere firing. Vatter's patents describe the metallizing of ceramic with iron, chromium, nickel, or tungsten, both with and without manganese (Ref. 6). Modification and improvement of these processes have continually evolved

(Refs. 7-11); however, this conventional moly-manganese seal is still the groundwork for a large segment of the industry today.

Continuing research and development have evolved additional joining techniques. Metallizing techniques with oxides, or mixtures of metals and oxides, have been described. The application of refractory metal oxides allows use of lower sintering temperatures (Refs. 12-15). Vapor deposition techniques have also been explored (Refs. 16 and 17). In general, these coatings tend to be spongy and difficult to wet with common brazing alloys. Furthermore, extensive wetting of the metallized layer will result in its being stripped from the ceramic (Ref. 18). Many metallizing techniques, consequently, use additional coatings over the metallizing layer of, commonly, nickel, copper, another electroplated layer, or a sprayed coating (Refs. 9, 19-24). Later techniques have used mixtures of oxides of ruthenium (RuO_2) and molybdenum (MoO_3) or rhenium (Re_2O_7), which were reduced to metal by wet hydrogen firing. Plasma spraying or flame spraying has proved applicable to the metallizing of ceramics both with and without flux oxide additions (Refs. 25 and 26).

Research directed toward the elimination of metallizing as a step in the joining procedure has, in general, emphasized the use of an active metal that will wet the ceramic. In early work, titanium or zirconium alloys, or hydrides of these metals, were used (Refs. 8, 10, 27-29). Later work

has shown that vanadium (Ref. 30), niobium, and tantalum can be used (Ref. 10).

Hot pressing of a composite of metal and ceramic has proved to be a successful method of seal fabrication. This technique has been undertaken with parts of finished size (Ref. 31), with powders that can be either pure or graded

in content across the seal (Refs. 32-34), and with niobium particles coated with alumina (Ref. 35).

A variety of other techniques, outlined in Table 1, have been tried experimentally, or on small parts or for low-temperature applications. Among these have been electron beam welding (Ref. 36), ceramic brazing (Ref. 37),

Table 1. Methods of ceramic-to-metal joining compared (Ref. 1)

Method	Classification ^a	Special processing conditions ^b	Important joint properties	General comments on use
(1) Hot-press bonding	One-step, solid phase	Medium-temperature pressing in neutral or reducing atmosphere.	Vacuum-tight, low-strength	Experimental, limited shapes
(2) Graded-power bonding	Two-step, solid phase	Cold compacting, medium- to high-temperature sintering in reducing atmosphere.	Vacuum-tight, usually low-strength	Experimental, limited material combinations
(3) Gas-pressure bonding	One-step, solid phase	High-temperature processing in autoclave.	Vacuum-tight, strength unknown	Experimental, complex precise shapes
(4) Active-metal brazing	One- or two-step, liquid phase	Medium- to high-temperature firing in high vacuum.	Vacuum-tight, high-strength	Commercial, limited by process sensitivity
(5) Electron beam welding	One-step, liquid phase	Controlled-vacuum fusion by intense electron beam.	Susceptible to massive cracking	Experimental, small joints only
(6) Glass soldering	One-step, liquid phase	Low- to medium-temperature firing in a slightly oxidizing atmosphere.	Vacuum-tight, strength limited by glass	Commercial, low temperature applications
(7) Ceramic brazing	Two-step, liquid phase	High-temperature firing in a neutral or reducing atmosphere.	High-temperature, high-strength, and vacuum-tight	Experimental, limited materials selection
(8) <i>In situ</i> ceramic firing	Two-step, liquid phase	Cold compacting, medium-temperature sintering in an oxidizing or reducing atmosphere.	Shrinkage causes some leaks and weakness	Experimental, limited to one ceramic composition
(9) <i>In situ</i> glass devitrifying	Two-step, liquid phase	Medium-temperature firing in an oxidizing or reducing atmosphere.	Properties depend on amount and composition of crystallized phase	Developmental, possible wide applications
(10) Refractory metal powder coating	Multi-step, metallizing	Powder deposition, high-temperature firing in a slightly oxidizing atmosphere, plating.	Similar to (4)	Widely used, versatile shapes and materials
(11) Metal/glass powder coating	Two-step, metallizing	Powder deposition, low- to medium-temperature firing.	Usually not vacuum-tight, low-strength	Widely used, versatile, low cost
(12) Metal/metal-oxide powder coating	Multi-step, metallizing	Powder deposition, medium-temperature firing in an oxidizing, followed by reducing, atmosphere.	Similar to (11)	Commercial, limited material combinations
(13) Refractory metal-oxide powder coating	Multi-step, metallizing	Powder deposition, medium-temperature firing in a reducing atmosphere.	Similar to (4)	Developmental, could replace (10)
(14) Refractory metal salt coating	Multi-step, metallizing	Salt deposition from solution, medium-temperature firing in a reducing atmosphere, plating, grinding.	Similar to (4)	Commercial, could replace (10)
(15) Condensed vapor coating	Two-step, metallizing	Masking, high-temperature vaporizing.	Similar to (4)	Development. limited to certain shapes, could replace (10)

^aNumber of steps does not include parts processing, assembly, metal-to-metalize joining, or disassembly.

^bLow Temperature: < 450°C

Medium Temperature: > 450°C; < 1250°C

High Temperature: > 1250°C

diffusion bonding (Refs. 38 and 39), ultrasonic joining (Ref. 40), and electroforming (Ref. 41).

B. Summary and Recommendations

Three types of metal-to-ceramic seals have been evaluated sufficiently for conclusions to be drawn on their applicability to thermionics: (1) alumina metallized with tungsten or molybdenum and subsequently brazed to a refractory metal, (2) alumina brazed to a refractory metal with an active braze alloy, and (3) niobium joined to alumina through a graded boundary layer.

The most successful metallizing techniques for alumina have been the use of fluxing oxides (alumina, calcia, or yttria, or combinations of these) with tungsten. Agreement exists among the organizations of Gulf General Atomic, Inc., General Electric Company, and Los Alamos Scientific Laboratory that a good metallizing base can be produced with the tungsten-yttria mix. The current state-of-the-art in the metallizing part of seal fabrication appears satisfactory for thermionic application.

Brazing of these surfaces to a refractory metal for elevated temperature application has proved difficult. A copper braze is limited to a temperature of 600°C because of cesium attack. Palladium becomes porous from Kirkendall-type effects after long-term heating in the 1000°C range. Initial data on the ruthenium-molybdenum eutectic indicate satisfactory performance above 1000°C but are too limited for definite conclusions to be drawn at present. Phase diagram information indicates the possibility of sigma phase formation in this alloy that could lead to cracking and bond failure.

The current state-of-the-art of brazing refractory metals to metallized surfaces shows attainment of a satisfactory high-temperature joint difficult at best. Satisfactory braze joints have been made with alloys with higher melting points than copper but have usually required the preplacement of a limited amount of braze alloy to prevent the formation of extensive brittle zones or Kirkendall-type defects. This technique precludes the production of filleted joints and makes the use of tapered joints desirable to distribute stresses. The only braze alloy that has been explored which offers a possibility of flow-brazing is the molybdenum-ruthenium eutectic. Additional work on this type of alloy to determine its long term stability under thermionic conditions appears to be justified.

Active metal braze techniques have been, in general, successful only with moderate-purity alumina and not with the high-purity alumina required for thermionic

applications. The general tendency of these braze alloys to continue reaction with the ceramic as a function of time can result in weakening or even fracturing the bond between the metal and the ceramic. This reaction tendency has been observed even with some alloys of vanadium that were designed for application to a metallized ceramic. Careful evaluation of this type of braze alloy is required for long test times to determine its applicability to thermionics. Of the available sealing techniques, active metal seals appear to offer the least chance of satisfactory performance.

The most successful seal fabrication technique with regard to temperature of application and to cesium corrosion has been the niobium-alumina graded seal. The usefulness of this seal is again limited by the production of porosity from Kirkendall-type diffusion effects at the point where the niobium is joined to another refractory metal, since this sealing technique has been evolved only for the niobium-alumina combination. For 10,000-h applications, the temperature above which porosity production could be estimated to limit the life of the seal would be—based on self-diffusion data for niobium—above 1000°C.

The only other approach to the metal-to-ceramic seal problem that might provide a satisfactory seal is *cermetizing*, or the use of a molten oxide eutectic rather than a metal to provide the seal. Little work has been done in this area. The temperatures required for this method and the stresses from thermal expansion mismatch may limit the success of the process.

The major limitation at present to the life of the seal in a thermionic diode appears to be irradiation damage. While data are being accumulated, the question of seal life under fast flux, long-time exposure is still very much open to question. Should irradiation damage to high-purity alumina, which is currently being used, prove to limit the life of the seal, a cubic-crystal-structure material such as stabilized zirconia could be used to advantage.

II. Techniques Currently Used in Thermionic Diodes

A wide cross section of the available seal fabrication techniques is currently being used in the fabrication of thermionic devices. Some of these techniques are summarized here.

A. Externally Fueled Diodes

Early tests of these diodes used moderate-purity alumina metallized with tungsten and brazed. The moderate

purity of the alumina improves the quality of the metallizing but opens the question of corrosion resistance under lengthy testing. No corrosion of this type of seal was observed during shorter testing periods. Current testing is being carried out with graded alumina-niobium seals, which are indicated to be among the best state-of-the-art seals.

B. Single Cell Thermionic Elements

High-purity alumina metallized with tungsten-yttria is a current metallizing process that has been shown by Battelle, GE, and Los Alamos to be among the best metallizing techniques available. As with all metallized seals, the performance limitation is imposed by the braze alloy. In this case the braze alloy, copper-nickel, has questionable reliability above 600°C under long testing periods. Below this temperature, reliability has been excellent.

Braze alloys at higher temperature are currently being evaluated under seal development programs. When sufficient testing has been completed to qualify a higher temperature braze alloy for seal application, its application to tungsten-yttria metallized seals appears justified for providing additional temperature margin.

C. Multiple Cell Thermionic Elements

This design of thermionic elements imposes lesser demands on seal performance than do other designs and, in turn, allows the selection of seals that have been proved in numerous applications and fabricated by well established techniques. Seals are of the molybdenum-metallized copper braze design. The molybdenum metallizing layer has generally been found to have lower bond strength to the ceramic than do the tungsten metallizing layers. The temperature is limited to the 600°C region because of the copper braze.

III. Materials Suitable for Thermionic Applications

The materials for metal-to-ceramic seals for application to thermionics are restricted by corrosion, by temperature, and by nuclear radiation environment. Small amounts of silicon dioxide in the ceramic cause attack by cesium vapor at temperatures above 600°C (Refs. 42-44). In addition, manganese oxide and titanium oxide have also been reported susceptible to cesium attack at thermionic temperatures (Ref. 45). Selection of brazing alloys is similarly restricted owing to corrosive attack of alloys containing some of the noble metals (Ref. 44). Additional limitations are imposed by thermal expansion coefficients, since thermal cycling of seals containing materials with significant

mismatch of thermal expansion characteristics results in seal failure, usually in the ceramic (Ref. 37).

The refractory metals are the primary materials of construction in a thermionic device, i.e., vapor-deposited-tungsten emitters and molybdenum or niobium collectors. The ceramic must be selected to match the thermal expansion characteristics of these materials. Figure 1 indicates that alumina or beryllia provide the closest match. At lower temperatures, the thermal expansion mismatch of zirconia and hafnia are only slightly greater than alumina or beryllia.

Most of the research effort has been directed toward alumina, apparently because of (1) its expansion characteristics, (2) its irradiation damage resistance as compared with beryllia, (3) its thermal shock resistance as compared with zirconium oxide and hafnium oxide, (4) its lack of toxicity problems, and (5) the general accumulation of

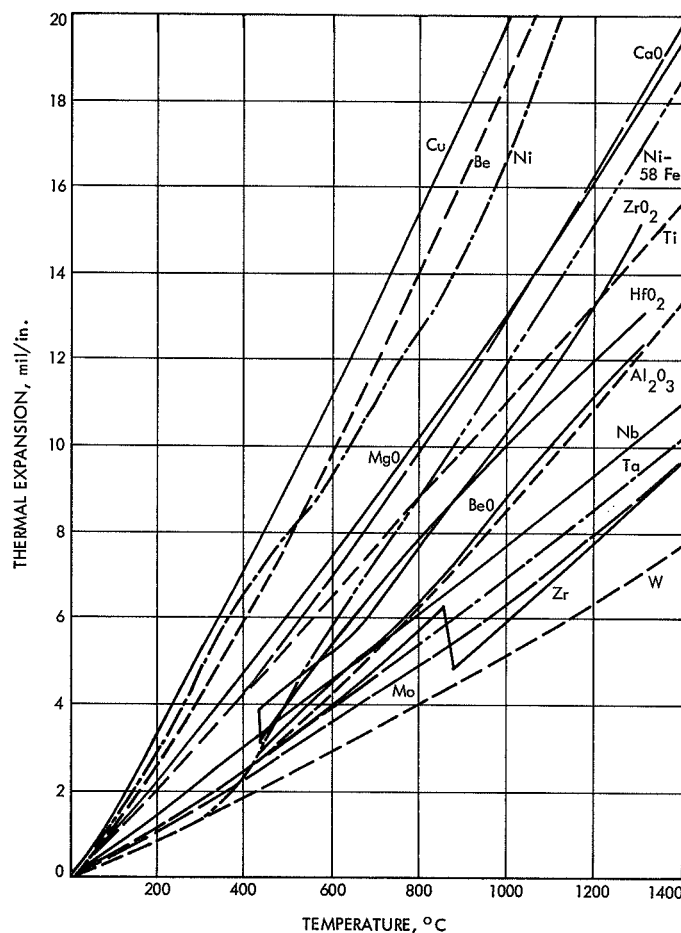


Fig. 1. Thermal expansion of some metals and ceramics (Ref. 51)

data resulting from its availability over a long period of time. A study of seals for thermionic converters by Levinson (Ref. 46) led him to conclude that "alumina is the most desirable insulator material and the principal current temperature limitation is imposed by brazing processes rather than the insulator material."

The problem of metal-to-ceramic seal production for thermionics can be defined as the metallizing and brazing, the active metal brazing, or the bonding of an oxide ceramic containing no silica, titania, or manganese oxide to a refractory metal.

IV. Metallizing of Ceramics

Numerous studies have been undertaken to explore the bonding mechanisms between a metallized layer and the bare ceramic. In low-purity alumina, most experimental work indicates bonding by the formation of a low-melting-point oxide phase, or *glassy phase*. The glassy phase results from the fluxing constituents added to the ceramic and aids densification. The best bonds were obtained with the maximum amount of glassy phase (Refs. 13, 47, 48). This phase was found to move into the pores of the metal layer and also to corrode the ceramic surface. With increased firing time, an increase in the amount of alumina dissolution by the glassy phase results in crystallization of galaxite and then corundum which, in turn, reduces the amount of glassy phase and weakens the bond. It has also been found that sintering temperatures must be high enough to cause the metallizing particles to form a coherent layer (Ref. 49). Infiltration of the sintered layer by the glassy phase has been proposed as a primary bonding mechanism known as the *glass migration theory of adherence* (Ref. 50). Excessive migration of the glassy phase results in coating of the particles in the metallizing layer to an extent that a strong bond between the metallizing coating and the braze alloy is excluded (Refs. 49 and 51).

Other observations of the metallizing layer interface revealed that (1) oxidation of the metallizing metal must be controlled, (2) chemical reaction between the metal oxide and the ceramic must form an interface zone, and (3) bonding between metal and ceramic through the interface must produce a graded, continuously coherent structure. Oxygen for the oxidation of the metallizing metal in hydrogen at high temperature was believed to have come from dissociation of impurity oxides in the ceramic. These ideas form the basis for what has been termed the *alumina reaction theory of adherence*.

It has been found that although high-purity alumina can not be wetted by either pure molybdenum (Ref. 50)

or pure tungsten (Ref. 51) it can be wetted by molybdenum oxide easily (Ref. 14). This has been attributed to chemical reaction or chemical complex formation between MoO_3 and Al_2O_3 . Similar adherence is possible using WO_3 (Ref. 45). These two oxides appear to be unique in wetting capability, since attempts to use the oxides of chromium, ruthenium, rhenium, or uranium were unsuccessful. After wetting the base ceramic, the oxide can be reduced to pure metal by hydrogen firing, which results in a density increase in excess of 100%. The coating produced is spongy and has a tendency to crack or peel (Ref. 24). The spongy layer is resistant to wetting by normal braze alloys, while alloys which will wet the metallizing layer tend to alloy with it stripping it from the ceramic. Circumvention of this problem is usually undertaken by electroplating the layer with nickel or reducing with hydrogen the nickel oxide applied to the spongy layer. The nickel layer is readily wetted by braze alloys. This technique, which was state-of-the-art during early thermionic diode testing, is limited to 600° to 750°C in converter applications (Ref. 42) when copper is used as the braze alloy.

Subsequent work on this problem has shown that hydrogen reduction of mixtures (by weight) of RuO_2 -60 MoO_3 , RhO_2 -60 MoO_3 , or Re_2O_7 applied to the spongy refractory layer will produce a wettable surface without damage to the spongy layer (Ref. 24).

The cracking or peeling problems associated with reduction of refractory metal oxides, powdered tungsten, or molybdenum metal may be avoided with an addition of other oxides or fluxing agents to wet the ceramic. The oxides are selected to produce a molten phase at metallizing temperatures that wets the ceramic and bonds the metallic layer of molybdenum or tungsten to the ceramic. Thermal expansion coefficients should be compatible with both the metallizing layer and the base ceramic. The fluxing layer should also be thermally stable during subsequent high-temperature exposure. The most commonly used oxides are Al_2O_3 , CaO , MgO , or Y_2O_3 .

Work undertaken at The Bendix Corporation (Ref. 38) involved a tungsten-yttria combination which, when applied to high-purity aluminas as a metallizing slurry and subjected to cross-bending tests, showed bond strength in excess of the ceramic. ASTM tensile tests confirmed the cross-bending tests.

Tests of a molybdenum-yttria mix that was formulated and applied in the same way as the tungsten-yttria mix showed low bond strengths. It was theorized that grain

growth in the molybdenum-yttria system at sintering temperatures prevents the larger molybdenum particles from being transported into the ceramic grain boundaries to form an anchor for the metallizing layer.

The most promising metallizing composition was W-2 Y₂O₃. This slurry was applied to the 99.5%-purity alumina by brushing and the pieces were sintered in wet hydrogen (dewpoint + 35°C) at 1650°C for 45 min.

Similar work at Battelle sponsored by the Air Force (Ref. 52) on the bonding of refractory metals to yttria with an intermediate foil layer of yttrium metal oxidized to Y₂O₃ met with success (Table 2). Five thermal cycles between 400° and 2500°F did not affect the bonds. Corrosion by cesium was not tested.

Cowan and Stoddard (Ref. 45) successfully metallized alumina with tungsten metal when the ceramic contained 0.05 to 2.0 Y₂O₃. The yttria addition, however, results in a decrease in density and a loss in strength in the ceramic. Bond strength was 7700 psi after a wet-hydrogen sintering treatment at 1600°C and 9000 psi with a treatment at 1700°C.

Work on fluxing additions of oxides of aluminum (Al₂O₃), barium (BaO), calcium (CaO), magnesium (MgO), and yttrium (Y₂O₃) to metallizing mixtures has been actively pursued at GE under Bureau of Ships contracts (Refs. 53 and 54). Work on barium oxide was discontinued

early in the program when it was shown to be unstable. The compositions investigated are shown in Table 3.

The first coatings studied were molybdenum-based and contained oxides that formed a ternary eutectic liquid of MgO-CaO-Al₂O₃ at the sintering temperature. The ternary eutectic was initially chosen to provide a liquid phase at a low temperature (1345°C). Later, it was determined that coatings containing binary mixtures of CaO and Al₂O₃ possessed structures and properties very similar to coatings containing ternary oxide compositions. Furthermore, it was found that at the sintering temperature that was required to form the desired oxide phase at the interface, extensive densification of the molybdenum coating occurred regardless of whether a binary or ternary oxide composition was used.

It was also determined that trace impurities in the base ceramic altered the melting behavior of the oxide eutectic. This, in turn, affected the quality of the metallizing layer since the eutectic-liquid phase fills the interstices of the sintered metal layer and then solidifies, either through cooling or through continued reaction with the alumina which raises the melting point of the eutectic.

Firing at 1800°C produced a molybdenum layer well interlocked with the fluxing eutectic layer. The fluxing layer, however, was not well bonded to the ceramic, and the structure consequently had low strength. An increase in the sintering temperature to 1850 or 1900°C produced a denser molybdenum layer, eliminated interface failures, and yielded leak-proof samples.

Similar metallizing compositions were explored at Westinghouse (Ref. 55) where material was sintered in N₂-25 H₂ at 1675°C for one-half hour. It was concluded that "these metallizing paints had insufficient adherence to high alumina ceramics for practical usefulness." This conclusion apparently agrees with the GE work that higher sintering temperatures were needed for adequate bonding.

The work at GE also included mechanical testing of bond strength. These adherence tests, as well as occasional failure at the metallizing-ceramic interface after high-temperature testing, showed that less than optimum bonding was obtained with coatings in which the metallic phase sintered so densely that mechanical interlocking of the oxide phase with the metal phase was reduced. It was believed that although chemical bonding may play a role in achieving vacuum-tight structures, mechanical bonding contributes a greater part of the adhesive strength of a metallizing coating.

Table 2. Results of bonding yttria to refractory metals with an yttrium transition layer (Ref. 52)

Refractory metals	Bonding temperature, °F	Bonding pressure, psi	Time, h	Thickness of yttrium foil, in.
Tungsten	2200	2500	2	0.003
	2200		2	0.001
	2550		2	0.003
	2550		2	0.003
Rhenium	2550		2	0.003
	2550		1	0.001
	2700		2	0.003
W-10 Re	2550		2	0.003
	2550		1	0.001
	2700		2	0.003
TZM	2200		2	0.003
	2200		2	0.001
	2550		2	0.003
	2550		2	0.003

All metals produced successful bonds with the use of graphite dies.

Table 3. Effect of oxide additions to metallizing compositions (Ref. 53)

Mix number	Metal, vol %	Oxide composition, wt %					Sintering temperature, °C for 1 h	Number vacuum-tight	Number leaking
		Al ₂ O ₃	CaO	MgO	BaO	Y ₂ O ₃			
1	65 Mo	51.8	41.5	6.7	—	—	1610	0	6
							1680	0	6
							1750	3	1
							1755	5	1
							1760	3	0
							1800	3	0
							1850	7	0
18	65 Mo	80.0	17.0	3.0	—	—	1700	0	3
							1750	0	3
							1800	0	6
							1850	3	0
							1900	3	0
21	65 Mo	95.0	4.3	7.0	—	—	1700	0	2
							1750	0	3
							1800	3	3
							1850	1	2
							1900	0	3
36	65 Mo	80.0	20.0	—	—	—	1700	0	3
							1750	0	3
							1800	1	5
							1850	3	0
							1900	3	0
54	65 Mo	60.0	—	—	40	—	1750	0	3
55	65 Mo	65.0	—	—	—	35	1800	3	0
							1850	2	1
							1900	3	0
56	98 Mo	—	—	—	—	100	1890	0	3 ^a
60	98 W	—	—	—	—	100	1890	2	1 ^a

^aMetallized layer was not nickel-plated before brazing; other samples were.

Several methods for controlling the density of the sintered metallic layer were then investigated, including the use of tungsten instead of molybdenum to reduce the sintering rate, and the control of the melting behavior of the bonding oxide addition through chemical composition and precalcination.

The metallizing mixes investigated under this part of the program are shown in Table 4. From their vacuum tightness, peel strength, and microstructural appearance, most of the coatings applied to bodies of silica-free alumina were acceptable and several were excellent. Although relatively few specimens of each type were examined, the estimated order of preference of the metallizing mixes shown in Table 4 would be coatings No. 60, 154, 155, 169, 175, 176, 192, and 193. Fewer coatings were deemed acceptable when sintered into Lucalox-type high-purity alumina. Several, however, were considered quite satisfactory and yielded reliable seals, including 169, 175,

and 176. These three coatings are tungsten with additions of alumina, alumina with calcia, and alumina with yttria.

V. Brazing of Metallized Ceramics

Composition, flow, and melting points of commercial braze alloys are readily available, having been published in a variety of compendia (Refs. 56 and 57). Data are also available as the result of more recent investigations (Refs. 58–61). Data on physical properties, such as thermal expansion, are seldom available nor are data on mechanical properties.

The selection of a braze alloy for thermionic applications is generally based on

- (1) Resistance of the bonds to cesium vapor.
- (2) Capacity of the metallic member to be wetted without serious attack.

Table 4. Tested metallizing compositions, by weight (Ref. 54)

Composition number	Molybdenum MGR, Type P	Tungsten 5 μ m	Tungsten 2 μ m	Alumina Linde A	Alumina A-14-325 mesh	Calcium carbonate	Yttrium oxide	Composition number	
								114	117
36	80.0			13.8		6.2			
60		98.0					2.0		
73		94.2			4.0	1.8			
114					85.9	14.1			
115		95.2						4.8	
117					50.6	49.4			
118		95.2							4.8
154			94.3		4.0	1.8			
155			95.2					4.8	
163			98.1			1.9			
169			95.1	4.9					
175			95.8		4.1	0.1			
176			95.2		4.7		0.1		
190			100.0						
191	100.0								
192			97.9		2.05	0.05			
193			97.6		2.35		0.03		
194	33.9		63.33		2.7	0.07			
195	33.9		62.93		3.1		0.07		

All compositions heated first for 2 h at 1200°C, then 2 h at 1400°C.
Numbers 169, 175, and 176 yielded satisfactory and consistently reliable seals on Lucalox high-purity alumina.

(3) Capacity of the metallized layer to be wetted without deterioration of its adherence to the ceramic or the properties of the ceramic.

(4) Compatibility of thermal expansion coefficients of the ceramic and metal.

(5) Ductility sufficient for the fabrication of wire or foil.

(6) Freedom from brittle phase formation.

Initial work in the thermionics field used copper brazing of a metallized layer made wettable by hydrogen sintering of an electroplated layer of nickel or copper. This seal was recognized to have an absolute temperature limit of 900°C but long-term cesium exposure reduced the limit to 600°C (Ref. 42).

The resistance of gold and silver to corrosion eliminates them from consideration. The use of iron, nickel, or cobalt base alloys in conjunction with refractory metals can result in formation of reduced melting-point eutectics or brittle compound formation (Table 5).

Table 5. Minimum melting point and compound formation in the refractory metal-cobalt, -iron, -nickel, and -palladium systems (Ref. 62)*

Metal	Minimum melting point, °C			
	Molybdenum	Niobium	Tantalum	Tungsten
Chromium	—	1660	1700	>1845
Cobalt	1340	1235	1276	1480
Iron	1450	1360	1410	1525
Nickel	1315	1100	1360	1452
Palladium	—	1560	—	>1547
Metal	Compound			
	MoCr ₂ , MoCr ₃ , MoCr ₅	NbCr ₂	TaCr ₂	?
Chromium	Mo ₂ Cr ₃			
Cobalt	MoCo ₃	NbCo ₂	TaCo ₃	WCo ₃
	Mo ₅ Co ₇		TaCo ₂	W ₆ Co ₇
Iron	Mo ₂ Fe ₃	Nb ₂ Fe ₂	TaFe ₂	WFe ₂
		NbFe ₂		W ₂ Fe ₃
Nickel	MoNi ₃	NbNi	TaNi	WNi ₄
	MoNi ₄	NbNi ₃	TaNi ₂	
	MoNi		TaNi ₃	
			Ta ₃ Ni ₂	
Palladium	None	NbPd ₃	None	None

*From *Constitution of Binary Alloys, First Supplement* by R. P. Elliott. Used with permission of McGraw-Hill Book Company.

Nickel has been found to readily alloy with molybdenum metallizing, stripping it from the ceramic. Thus the amount of nickel must be minimized (Ref. 38). Iron and cobalt wet molybdenum metallizing, but thermal expansion mismatch has caused the ceramic to fracture (Ref. 38). Extensive brittle compound formation, which occurs with chromium as a result of exposure to continued high temperature, renders the seal susceptible to cracking. The cracking might be reduced by lowering the amount of chromium.

Results on specific braze alloys, based on cobalt, chromium, iron, nickel, or palladium (by weight) tested in the GE program (Ref. 54), are summarized:

- (1) Cr-50 Ni. Brittle phase formation tendency could be inhibited by holding at about 1600°C. Considerable reaction occurred with niobium and tantalum at this temperature, and pore formation and reaction that occurs with molybdenum was believed too extensive for successful sealing to molybdenum-based metallizing.
- (2) Cr-78 Fe. Formed brittle phases with molybdenum and tantalum, and penetrated excessively into niobium.
- (3) Cr-40.6 Pd. Did not flow into the joint; reacted excessively with molybdenum.
- (4) Cr-48 Pd-32 Ni. Formed brittle phases and penetrated excessively into niobium.
- (5) Nb-33 Cr-33 Ni. Did not exhibit good flow, and formed brittle phases with tantalum and molybdenum. With niobium, when complete flow was realized, bonds of good quality were obtained. The following three braze compositions exhibited more promising results.
- (6) Cr-62 Pd. Produced its best appearing bonds when bonding molybdenum to molybdenum or to tungsten. Increasing the brazing temperature from 1500° to 1600°C for niobium to molybdenum caused good appearing bonds to change to a porous structure. Similar results were obtained with tantalum to molybdenum. Bonds formed between tungsten and tungsten-based metallizing brazed at 1500°C were intact and pore-free, but the ceramic cracked severely from stresses caused by the poor thermal-expansion match between the tungsten and the alumina ceramic.
- (7) Nb-30 Pd-20 Ni. Formed good appearing bonds when brazing molybdenum to molybdenum, molybdenum to tungsten, and tungsten to tungsten.

Good bonds were also obtained when brazing tantalum and niobium to molybdenum. However, at a 1500°C considerable reaction occurred between the braze and the niobium, or tantalum if an excess amount of braze was present. When brazing niobium or tantalum to a surface metallized with tungsten, pores formed at the interface.

- (8) Nb-33 Fe. Performed satisfactorily with niobium, tantalum, or molybdenum with a brazing temperature of 1670°C. Lower temperatures caused brittle-phase cracking problems. A braze made between tungsten and molybdenum was free of cracks, but developed some pores. Such pores did not form when molybdenum was brazed to a surface metallized with tungsten, but pores did form with niobium (and to a lesser extent with tantalum) when it was brazed to such a surface. This braze also formed leak-tight seals to bare ceramic as an active-alloy type of braze. However, these bonds were quite weak—apparently from the lack of mechanical interlocking that is obtained with brazing on a metallized surface.

Palladium has also been evaluated as a braze material. As shown in Table 5, a brittle phase occurs with niobium but not with the other refractory metals (Ref. 62). The continued exposure of molybdenum to high temperature caused pore formation, apparently due to Kirkendall-type effects, that disrupted the metallizing (Ref. 53). This process could be reduced to an acceptable level by sparing use of the braze metal.

Seals were fabricated at Los Alamos with palladium and Palco (palladium-cobalt). The brazing technique had poor reliability (Refs. 63 and 64). Of six samples tested at 1100°C for 2000 h, only one sample remained vacuum-tight. Evaluation of the tests indicated pore formation, consumption of the tungsten metallizing, and loss of bonding.

Vanadium was also evaluated as a braze alloy. It was found to be very aggressive, in that no trace of the tungsten metallizing layer was found after the brazing. Because of the aggressiveness, very short braze cycles and high heating rates were required. This resulted in a large number of failures due to cracked ceramics. Lucalox brazed to Nb-1 Zr samples with vanadium survived 2000 h, or to 1100°C. Results of tests on other braze alloys are summarized in Table 6.

A V-30 Nb-5 Ti alloy was evaluated by C. M. Cappelletti (Ref. 30). This composition was derived from

Table 6. Ceramic-metal wetting tests (Refs. 63, 64)

Braze alloy, wt %	Ceramic type ^a	Brazing temperature, °C	Results
Vanadium	Al-14 ^b	1960	Wet both metal and ceramic well. Considerable alloying with metal. No evidence of metallized coating after brazing.
Vanadium	Lucalox ^b	1960	Same as above.
Palladium	Al-14 ^b	1590	Wet both metal and metallized ceramic well. Considerable alloying with metal. Metallized coating still intact.
Pd-35 Co	Al-14 ^b	1260	Wet both metal and metallized ceramic well. Considerable alloying with metal. Metallized coating still intact.
V-32 Nb-10 Ti	Al-300	1800	Good wetting of ceramic and metal. Limited alloying with metal (0.003 in.) and limited intergranular attack of ceramic.
V-32 Nb-10 Ti	Lucalox	1800	Fair wetting of ceramic, good wetting of metal.
Ti-10 Nb-12 V-9.5 Cr-2.5 Al	Al-14	1700	Good wetting of metal, extensive intergranular attack of ceramic.
Ti-19 Nb-12 V-9.5 Cr-2.5 Al	Lucalox	1700	Good wetting of metal, fair wetting of ceramic.
Zr-0.5 Ni	Al-14 and Lucalox	1830	Good wetting of metal, but severe attacking of ceramics.
Cobalt	Al-14 ^b	1540	Extreme alloying with the metal. Wet metallized ceramic well.

^aAl-14 ceramics were fabricated by pressing Al₂O₃-0.5 Y₂O₃ (by weight).
^bTungsten-metallized ceramics.

the minimum-melting-point composition in the V-Nb-system, which could not be worked into wires unless its ductility had been increased by a 5 Ti (by weight) addition. The V-30 Nb-5 Ti was found to wet Nb-1 Zr well without series attack, but penetrated through the tungsten-metallizing layer. The resulting seal was considered a compromise solution between a metallizing-plus-brazing joint and an active metal seal, with the metallizing fulfilling two functions: it enhanced the entry of the fused alloy into the brazing gap, and it protected the ceramic against too violent an attack from the active components of the brazing alloy.

The samples brazed with Cu-2 Ni ruptured completely in the ceramic. Those brazed with palladium had an average tensile strength of about 10 kg/mm², but the batch with the shorter brazing time showed a larger scattering of the values. All palladium-brazed samples ruptured between the ceramic and metallized layers, leaving a clean and undamaged ceramic surface. Thermal cycling tests on samples between 500° and 1200°C at 50°C/min heating rate and 200°C/min cooling rate did not produce failure in 100 cycles.

The V-30 Nb-5 Ti brazed samples, in contrast with the palladium brazing, indicated the weakening of the ceramic by the action of the active components of the brazing alloy. Results of tests are summarized:

Braze washer and conditions	Tensile strength of vacuum-tight samples, kg/mm ²		
	Average	Highest	Lowest
Cu-2 Ni, 60-μm thick 1150°C, Mo furnace			
180 s, 5 of 6 v-t	14.3	15.6	12.6
Palladium, 60 μm 1570°C, Mo furnace			
90 s, 6 of 6 v-t	9.6	11.0	8.3
20 s, 5 of 6 v-t	10.0	13.6	6.8
V-30 Nb-5 Ti, 80 μm 1805°C, Ta furnace			
60 s, 3 of 6 v-t	8.4	8.6	8.1

The use of rhenium as a braze alloy resulted in loss of bonding due to Kirkendall-type effects with surfaces metallized with either molybdenum or tungsten (Ref. 24). Satisfactory joints have been formed with the eutectic composition of ruthenium and molybdenum (Ru-58.4 Mo, by weight). The braze alloy was prepared from the oxides, and brazed in hydrogen to reduce the oxides to metal,

form the alloy, and complete the seal. Brazing temperatures were just above the melting point (1945°C) with no holding time. The seals were heated to 1800°C without loss of vacuum integrity. No evidence of attack was observed when the seal was exposed to cesium for 1400 h at "incandescent temperatures."

VI. Diffusion Bonding

Alumina-niobium bonds have been successfully formed at Battelle by means of gas pressure bonding techniques, or autoclaving (Ref. 65) at 2200°F under a pressure of 10,000 psi. Work at Solar showed that the pressure requirements can be reduced by the use of an intermediate foil of material with a lower melting point (Ref. 66).

The process has been evaluated at GE for application to thermionics (Refs. 53 and 54). Palladium, nickel, and chromium, used as the intermediate foils in a structure of molybdenum- or tungsten-metallized ceramic joined to a refractory metal, were bonded with high pressure at a temperature below the melting point of the diffusing metal foil. Because a very close match was required between the bonded surfaces, the process was not applicable to sleeve-type joints.

The program evolved a process, similar to flow brazing, in which the pressure was eliminated and the temperature was raised above the melting point of the diffusing metal. The braze-diffusion-bonding process used a thin preplaced shim of braze alloy which controlled the extent of compound formation. Holding times allowed the braze alloy to diffuse into both the metallizing layer and the metal members.

A nickel shim provided excellent bonding between niobium and molybdenum (as a solid part or as a metallized surface), tantalum and molybdenum, molybdenum and molybdenum, molybdenum and tungsten, and tungsten and tungsten. Varying degrees of porosity occur at the interface when this technique is used for bonding niobium or tantalum to tungsten. Although "pores do not appear to develop when nickel braze-diffusion-bonding molybdenum to tungsten-based metallizing, more nickel intermetallic appears to form and seems to penetrate the molybdenum-grain boundaries more than when bonding molybdenum to molybdenum" (Ref. 53).

Braze-diffusion-bonding of molybdenum to tungsten metallizing layers caused the alumina to fracture as a

result of the high residual stresses produced by thermal expansion mismatch between the molybdenum and alumina. Similar problems were encountered when tungsten was bonded to a tungsten-metallized alumina ceramic.

VII. Active Metal Brazing

The term *active metal* is applied to those metals such as hafnium, niobium, tantalum, titanium, vanadium, yttrium, or zirconium that will wet a ceramic. Titanium and zirconium can be alloyed with copper, iron, or nickel without any loss in wetting ability.

The greatest problem area associated with active-metal alloy seals is the continued reaction of the alloy with either the metal or the ceramic member during elevated temperature exposure. While this continued reaction can strengthen the bond, it can also result in the formation of new phases, frequently intermetallics that are hard and brittle and unable to withstand the stresses imposed by differential thermal expansion of the seal components.

Numerous braze alloys have been found to produce satisfactory joints between refractory metals and ceramics in screening-type tests that evaluate only wetting and flow characteristics, and not stability at high temperature for long periods of time. Tests on a series of braze alloys at Oak Ridge National Laboratory (Ref. 58) yielded the results shown in Table 7. The conclusion drawn from these tests was that brazing alloys such as Ti-48 Zr-4 Be

Table 7. Wettability results of various brazing alloys on Al_2O_3 , UO_2 , BeO and graphite (Ref. 61)

Braze alloy, wt %	Brazing temperature, °C	Wetting ^a			
		Al_2O_3	UO_2	BeO	Graphite
Commercial alloys					
100 Cu	1100	None	None	None	None
Ni-Si-B (AMS 4778)	1040	↓	↓	↓	↓
Ni-10 P	1000	None	None	None	None
Au-18 Ni	1000	None	None	None	None
Nickel-clad Ti	1050	Good	Good	Good	Good
Experimental alloys					
Ti-49 Cu-2 Be	1000	Good	Good	Good	Good
Ti-28 Ag-4 Be	1100	Good	Fair	Fair	↓
Ti-48 Zr-4 Be	1050	Poor	Poor	Poor	↓
Ti-46 Pd-6 Al-2 Be	1150	Fair	Poor	Poor	↓
Zr-23 Cu-2 Be	1150	↓	Poor	Fair	↓
Zr-5 Be	1050	↓	Good	Poor	↓
Zr-6 Ni-6 Cr-6 Fe ^b	1150	Fair	Good	Poor	Good

^aGood—continuous filletting, extensive spreading; fair—intermittent filletting, little spreading; poor—no flow, wetting only at contact points.
^bBritish Patent 890,971.

and Ti-49 Cu-2 Be flow readily on oxides and graphite. No long-term stability testing or cesium compatibility testing was done. The purity of the alumina was not specified, but from the results of other investigators it would appear to have been of moderate purity.

Wetting tests on three active-metal braze alloys were run at Los Alamos Scientific Laboratory (Ref. 63). Results of these tests are included in Table 6. The V-Nb-Ti alloy flowed well on low-purity alumina but not on high-purity alumina, while the Ti-Nb-V-Cr-Al alloy displayed poor flow characteristics. Neither alloy produced consistent joints. Vanadium brazing on tungsten-metallized ceramics alloyed with the metallizing to an extent that no evidence of the metallizing remained. These brazes with Lucalox alumina and alumina-0.5 Y₂O₃ (by weight) were thermally cycled to 1100°C, held 100 h, cooled to room temperature, and then leak-checked. Twenty such cycles were completed without leakage.

Results of active-metal brazing investigations undertaken at The Pyromet Company are shown in Table 8 (Ref. 64). This table shows the complete lack of success with the high-purity alumina-yttria ceramic. Good results, however, were achieved with the Ti-48 Zr-4 Be when using a low-purity (97%) alumina.

At Westinghouse, P. E. Keuser et al. carried out a series of active-metal alloy brazing tests (Ref. 55). Alloys investigated are shown in Table 9. The alloys considered most satisfactory for use in conjunction with the moderate-purity alumina used in the tests were (by weight)

- (1) Zr-19 Nb-6 Be
- (2) Zr-48 Ti-4 Be
- (3) Zr-28 V-16 Ti

This selection was based on their ability to wet the ceramic, their good strength, and the hermetic property of the seals produced. Leak-check and modulus-of-rupture examples were prepared using the first two braze alloys for high temperature vacuum exposure and alkali metal exposure. Results of these tests are given in Tables 10 and 11. Although none of the samples survived the 1600°F potassium vapor, all survived the 1000°F test with the Zr-19 Nb-6 Be alloy sample displaying good strength.

VIII. Cermetizing

The name *cermetizing* was used by R. J. Kiwak (Ref. 37) for a joining technique based on the fact that molten

Table 8. Summary of brazing data, high-purity Al₂O₃-0.5 Y₂O₃ (Ref. 64)

Specimen number	Filler alloy	Brazing temperature, °F	Holding time, min	Results	
				Visual	Leak test
1	Ti-Zr-Mo-Fe	2280	5	Fillet, 90% complete	Gross leak
2	Ti-Zr-Mo-Fe	2440	None	Fillet, 50% complete	Gross leak
3	Ti-Zr-Mo-Fe	2300	1	Fillet, 50% complete	Gross leak
4	Ti-Zr-Mo-Fe	2290	5	Fillet, 100% complete	Gross leak
5	Ti-Zr-Mo-Fe	2280	5	Fillet, 100% complete	Gross leak
6	Ti-Zr-Mo-Fe	(Re-brazed at 2290)	5	Fillet, 100% complete	Gross leak
			2	Fillet, 100% complete	Gross leak
7	Ti-Zr-Be	2000	5	No fillet	Gross leak
8	Ti-Zr-Be	1970	5	No fillet	Gross leak
		(Re-brazed at 2000)	5	Fillet, 90% complete	Leak tight
9	Ti-Zr-Be	1970	7	No fillet	Gross leak
		(Re-brazed at 2350)	5	Fillet, 90% complete	Leaked at 5×10^{-5} cm ³ /s
10	Ti-Zr-Mo-Fe	1950	5	Fillet, 70% complete	Gross leak
11	Ti-Zr-Be	2140	5	Fillet, 50% complete	Leaked at 1×10^{-7} cm ³ /s
		(Re-brazed at 2350)	5	Fillet, 50% complete	Leaked at 1×10^{-7} cm ³ /s
12	Ti-Zr-Be	1950	5	Fillet, 80% complete	Gross leak
13	Ti-Zr-Be	2100	None	Fillet, 60% complete	Leaked at 1×10^{-6} cm ³ /s
14	Ti-Zr-Mo-Fe	2290	15	Fillet, 80% complete	Leaked at 1×10^{-6} cm ³ /s
15	Ti-Zr-Be	2300	None	Fillet, 50% complete	Ceramic cracked
16	Ti-Zr-Be	2100	15	Fillet, 30% complete	Leaked at 1×10^{-7} cm ³ /s

Table 9. Active braze alloy preliminary screening using Nb-1 Zr metal member with Wesgo alumina^a (Ref. 55)

Braze alloy, wt %	Brazing temperature, °F	VT ^b	Tensile strength, psi	Remarks
Zr-19 Nb-6 Be ^c	1940	4/4	9,750	Wets niobium alloy D-43 well
Ti-28 V-4 Be	2370	1/4 0/4	>240 ^d >4,475 ^e	Wets niobium alloy D-43 and tantalum alloy T-111 well
Zr-28 V-16 Ti ^c	2270	2/4	4,850	—
Ti-48 Zr-4 Be ^c	1940	4/4 4/4	4,900 9,575 ^e	Wets niobium alloy D-43 well
Ti-46 Zr-4 V-4 Be	1830	4/4 1/4	— 6,938 ^e	—
Zr-30 V-20 Nb	2415	0/4	140	—
V-35 Nb	3400			No test
Ti-30 V	3000			No test
Zr-25 V-15 Nb	2435	0/4	50	Forms skull on niobium alloy D-43 and tantalum alloy T-111
Zr-30 Ti-20 V	2480	0/4	>202	Forms skull on niobium alloy D-43 and tantalum alloy T-111, Nb-1 Zr alloy
Zr-30 Ti-30 V	2335	0/4	245	Wets niobium alloy D-43 and tantalum alloy T-111 well
Ti-35 V-30 Zr	2595	0/4	>500	—
Ti-30 Zr-20 V	2595			No test
Ti-30 V-8 Si	2480	0/4	>1,175	Wets niobium alloy D-43 and tantalum alloy T-111 well

Brazed in vacuum furnace (10⁻⁵ torr) at temperature indicated; no hold time. Results shown are from the best braze run for each alloy.

^aAl₂O₃-0.1 MgO-0.1 CaO-0.1 SiO₂.

^bNumber of vacuum-tight (helium leak rate of less than 1 × 10⁻⁹ torr-liter/s) over total number tested.

^cOne of 3 brazes and ceramic-to-metal assemblies considered most favorable for further evaluation in potassium, potassium-sodium eutectic, and lithium.

^dSymbol > indicates incomplete melting. Greater strengths might be expected with increased temperature but were not attempted because of excessive pressure in the furnace at elevated temperature.

^eMade with AD 99 alumina; 99% Al₂O₃.

oxides will wet metals much more readily than metals wet oxides.

It was found that Mo-Y₂O₃-Al₂O₃ cermets would sinter well to a molybdenum or other refractory metal substrate, especially in the presence of a liquid ceramic phase. The sealing technique consisted of cermetizing the refractory metal at temperatures as high as 1900°C in a furnace atmosphere of purified argon. Then the alumina-yttria eutectic (mp 1760°C) was melted between the alumina and the cermet layer on the metal. The eutectic adheres

to the alumina and infiltrates the porous cermet layer, forming a chemical as well as a mechanical bond. This process, called the *yttria fusion process*, is the complete reverse of standard practices. Only three constituents—molybdenum, yttria, and alumina—are found in the seal region, and all are resistant to corrosion by cesium.

IX. Graded Seals

This type of seal, usually formed by the gradation of materials used from ceramic to metal over a finite distance, can be produced by hot pressing or pressing and sintering the composite (Refs. 32, 33, 38, and 67). Initial work in this field required a gradual gradation and resulted in a seal that was quite long. When tungsten was used, the high tungsten portion of the seal did not densify adequately to be vacuum-tight. Increased sintering temperatures increased densification and produced vacuum tightness (Ref. 34) but distorted the seal. This was caused by a variation of sintering shrinkage with composition.

The problem was pursued at GE with work on composites of alumina-molybdenum. Initial studies (Ref. 53) produced vacuum-tight structures with a fixed ratio of alumina-molybdenum but not with a gradation of composition needed for a seal.

Follow-on studies (Ref. 54) produced graded vacuum-tight seals which were electrically insulating. These studies revealed the need for organic binders during pressing and indicated that the addition of yttria aided densification and mechanical strength. The cermet cylinders remained vacuum-tight after nine thermal cycles to 900°C followed by 327 h at 1250°C. The problem of length was not alleviated, since it was found that "Until practical methods for continuously varying the composition are developed, or until layers of quite uniform thickness can be loaded into a die, it appears necessary to use relatively thick layers in those regions most susceptible to failure—the central region" (Ref. 54).

Work on graded seals was pursued at GE (Ref. 34) with niobium rather than molybdenum or tungsten since the thermal expansion coefficient of niobium was close to that of alumina. Microprobe analysis of a ceramic-to-metal interface after 6 h at 1700°C showed a cross-diffusion of about 10 μ, with no significant interaction. This was judged to indicate stability for long times.

Niobium was directly bonded to high-purity Lucalox alumina; however "attempts to thermal cycle the direct-bonded members resulted in fracturing at the interface,

Table 10. Effect of potassium vapor exposure on the room temperature flexural strength of selected ceramic-metal sealing systems (Ref. 55)

Ceramic	Braze alloy, wt %	Brazing temperature, °F	Key ^a	Flexural strength, psi		
				As brazed	Vacuum-exposed 500 h, 1600°F	Potassium vapor 500 h, 1600°F
Wesgo Alumina (99.7-Al ₂ O ₃)	Zr-19 Nb-6 Be	1940	$\bar{x}$ s n	25,655 7,370 11	12,965 4,505 ^c 2	0 ^b — 4
	Ti-48 Zr-4 Be	1940	$\bar{x}$ s n	23,342 4,690 12	19,760 1,440 ^c 2	0 ^b — 4

All tests on modulus-of-rupture assemblies using Nb-1 Zr metal member.
^aThe symbol $\bar{x}$ = arithmetic mean, s = standard deviation; n = number of specimens tested.
^bNo modulus-of-rupture structures survived exposure test intact.
^cStandard deviation has little significance for sample size of two pieces.

Table 11. Effect of alkali-metal vapor exposure on the room temperature flexural strength of selected ceramic-metal sealing systems (Ref. 55)

Ceramic	Metal member	Braze alloy, wt %	Brazing temperature, °F	Alkali metal	Key ^a	Flexural strength, psi			Leak test, alkali-metal-exposed	Remarks: Room temperature flexural strength and leak tests
						As brazed	Vacuum-exposed, 500 h, 1000°F	Alkali-metal-exposed, 500 h, 1000°F		
Wesgo Alumina (99.7 Al ₂ O ₃)	Nb-1 Zr	Zr-19 Nb-6 Be	1940	Potassium ^b	$\bar{x}$ s n	25,655 7,370 11	21,100 3,300 ^d 2	21,432 2,250 3	3/3 ^c	Good results
	Nb-1 Zr	Ti-48 Zr-4 Be	1940	Potassium ^b	$\bar{x}$ s n	23,342 4,690 12	16,335 2,140 4	6,120 3,500 3	4/4 ^c	Fair results
	Nb-1 Zr	Zr-19 Nb-6 Be	1940	Sodium potassium ^d	$\bar{x}$ s n	25,655 7,370 11	22,100 3,300 ^d 2	9,587 1,320 4	4/4 ^c	Fair results
	Nb-1 Zr	Ti-48 Zr-4 Be	1940	Sodium potassium ^d	$\bar{x}$ s n	23,342 4,690 12	16,335 2,140 4	10,390 1,820 4	4/4 ^c	Fair results

All tests on modulus-of-rupture assemblies using Nb-1 Zr metal member.
^aThe symbol $\bar{x}$ = arithmetic mean; s = standard deviation; n = number of specimens tested.
^bOxygen level in associated purity-test capsule was less than 10 ppm.
^cHelium leak rate of less than 1×10^{-9} torr-liter/s.
^dOxygen levels in two associated purity-test capsules were less than 10 ppm.

probably caused by interface stresses. These stresses resulted from differential expansion augmented by the different thermal conductivity of the two materials" (Ref. 35).

Further studies led to the development of multilayer interfaces. The graded five-layer interface was made of blends of Linde A (Al_2O_3), 0.5 wt % magnesium oxide powder, and niobium powder, starting at 90 vol % niobium adjacent to the metal and ending at 10 vol % niobium adjacent to the Lucalox. Weighted quantities of powders are used; so each layer of the grading was approximately 0.003-in. thick when compacted to theoretical density. The assembly was sealed in vacuum by an electron beam closure-weld between the outer niobium ring and the niobium end caps. When the hot gas isostatic-pressure operation was completed, the bonded and densified seal was machined to its final configuration. Thermal stability tests performed on fabricated seals have shown the interface to remain stable after 100 cycles from 650° to 1450°C, using a cooling and heating rate of 300°C per minute.

A modification of the technique was evolved through the use of 50- μm -diameter niobium particles coated in a fluidized bed with alumina of varying thickness to obtain the desired ratio of alumina to metal. Seals fabricated with this material survived quenching from 1300°K, while seals produced by mixing of powders survived quenching from 1000°K. The coated-particle seals have been fabricated with an overall thickness of 0.040 in. and have been found to have a thermal conductivity of 0.6 times that of niobium. Electrical resistivity as a function of temperature is shown in Fig. 2.

X. Seals Using Oxides Other Than Alumina

A seal has been formed between tantalum and zirconia by heating to approximately 2248°K (Ref. 68). Yttria-stabilized zirconia and clean tantalum metal were placed vertically in contact, with the metal resting on the ceramic. The temperature was raised rapidly to 2248° $\pm$ 20°K, at which point the interface between the ceramic and metal was seen to flow together and form the bond. Subsequent reheating to temperatures greater than 2248°K did not cause bond rupture.

Seals were suspended in the induction field by their tantalum components and heated until failure occurred. Temperatures as high as 2663° $\pm$ 20°K were measured before the bond parted. When the seals were immersed in liquid nitrogen for brief periods, e.g., 1 to 5 min, structural integrity was maintained without fracture.

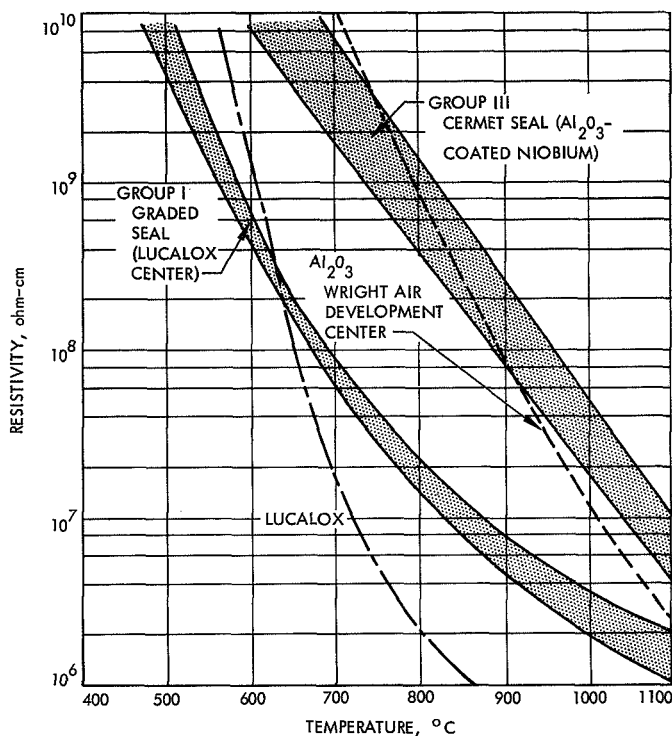


Fig. 2. Electrical resistivity of Lucalox-based seals as a function of temperature (Ref. 35)

Bonding intermediates, formed spontaneously at approximately 2248°K, were identified as tantalum zirconate ($\text{Ta}_2\text{Zr}_6\text{O}_{17}$); yttrium tantalate (YTaO_4); tantalum silicide (Ta_5Si); magnesium tantalate ($\text{Mg}_4\text{Ta}_2\text{O}_9$); aluminum tantalate ($\text{Al}_6\text{Ta}_4\text{O}_{19}$); and tantalum oxyfluoride (TaO_2F). It was established that the sealed zone holds a vacuum but that the zirconia itself permits a slow leak to atmospheric pressure, holding pressures (while pumping) of less than 10 μm .

Yttria was bonded to refractory metals with an intermediate layer of yttrium foil which was oxidized to Y_2O_3 (Ref. 52). This process was discussed in the previous section on metallizing with the results given in Table 2. Beryllia has been successfully joined to niobium, using active-metal brazing techniques (Ref. 55). Results of screening test are shown in Table 12. Samples were tested under vacuum at 1600°F and exposed to alkali metal vapors at 1600° and 1000°F. Results of these tests are given in Tables 13 and 14. The most successful of these tests were on Zr-28 V-16 Ti braze alloy used as an active-metal braze alloy.

XI. Corrosion Testing of Seals and Components

Many of the active metals that have poor corrosion resistance in the pure form, e.g., titanium or zirconium,

Table 12. Active braze alloy preliminary screening using Nb-1 Zr metal member with beryllia (Ref. 55)

Braze alloy, wt %	Brazing temperature, °F	Thermalox 998 (99.8 BeO)	
		VT ^a	Strength, ^b psi
Zr-19 Nb-6 Be ^c	1940	2/4	15,260
Ti-28 V-4 Be	2370	1/4	16,635
Zr-28 V-16 Ti ^c	2270	— ^d	15,740
Ti-48 Zr-4 Be ^c	1940	3/4	16,500
Ti-46 Zr-4 V-4 Be	1830		16,650
Zr-30 V-20-Nb	2415	3/4	15,175
V-35 Nb	3400		
Ti-30 V	3000		
Zr-25 V-15 Nb	2435		14,035
Zr-30 Ti-20 V	2480	0/4	>4,742 ^e
Zr-30 Ti-30 V	2335	4/4	13,165
Ti-35 V-30 Zr	2595	0/4	>10,280 ^e
Ti-30 Zr-20 V	2595		
Ti-30 V-8 Si	2480	4/4	8,370

Brazed in vacuum furnace (10⁻⁶ torr) at temperature indicated; no hold time. Results shown are from the best braze run for each alloy.

^aNumber of vacuum-tight over total number tested.

^bModulus-of-rupture and tensile.

^cOne of 3 brazes and ceramic-to-metal assemblies considered most favorable for further evaluation in potassium, potassium-sodium eutectic, and lithium.

^dVacuum-tight assemblies fabricated previously on Westinghouse SPUR program.

^eSymbol > indicates incomplete melting. Greater strengths might be expected with increased temperature but were not attempted because of excessive pressure in the furnace at elevated temperature.

when alloyed with other metals in an active braze alloy can have satisfactory corrosion resistance. This was illustrated by P. E. Kueser's tests on the Zr-19 Nb-6 Be braze alloy. Among the conclusions drawn from these tests was that "the micro structures of the 1000°F alkali metal vapor exposed seal systems showed no new details when compared to the 1600°F exposed specimens." Degradation of some of the alloys did occur, as shown by Tables 9 and 10. In some cases, this degradation was due purely to continued high temperature exposure; but in others, the process was accelerated by alkali metal exposure. Similar data are shown in Table 15 (Ref. 69). Where grain etching is reported, the effect is possibly due to a combination of temperature and poor quality vacuum rather than to alkali metal corrosion.

A literature survey was undertaken at GE on cesium vapor corrosion (Ref. 54). The data gathered and the results of corrosion tests undertaken are shown in Table 16. Follow-on contracts produced the corrosion results of Table 17. Three conclusions were drawn from these tests: (1) neither tungsten nor molybdenum metallizing were corroded by cesium, (2) the refractory metals were unaffected by cesium exposure, and (3) nickel-braze-diffusion bonds between refractory metals were not attacked.

XII. Irradiation Damage

An excellent, in-depth review of radiation damage to beryllia, alumina, and magnesia was written by R. S. Wilks (Ref. 78). Some of the most pertinent facts on cracking and failure are summarized in this section.

Table 13. Effect of vacuum and potassium-vapor exposures on the room temperature flexural strength of selected beryllia-metal sealing systems (Ref. 55)

Ceramic	Braze alloy, wt %	Brazing temperature, °F	Key ^a	Flexural strength, psi		
				As brazed	Vacuum-exposed, 500 h, 1600°F	Potassium vapor, 500 h, 1600°F
Thermalox 998 (99.8 BeO)	Zr-19 Nb-6 Be	1940	$\bar{x}$	15,404	17,300	<1,000 ^b
			s	1,220	800 ^c	—
			n	5	2	5
	Ti-48 Zr-4 Be	1940	$\bar{x}$	16,559	14,250	10,583 ^b
			s	2,500	—	3,740
			n	8	1	5
	Zr-28 V-16 Ti	2270	$\bar{x}$	13,503	13,985	11,810 ^b
			s	2,870	1,715 ^c	850
			n	6	2	5

All tests on modulus-of-rupture assemblies using Nb-1 Zr metal member.

^aThe symbol $\bar{x}$ = arithmetic mean; s = standard deviation; n = number of specimens tested.

^bAccompanying vacuum leak test assemblies broken during removal from capsule.

^cStandard deviation has little significance for sample size of two pieces.

Table 14. Effect of vacuum and alkali-metal-vapor exposures on the room temperature flexural strength of selected ceramic-metal sealing systems (Ref. 55)

Ceramic	Metal member	Braze alloy, wt %	Brazing temperature, °F	Alkali metal	Room temperature flexural strength, psi				Leak test, alkali-metal-exposed	Remarks: Room temperature flexural strength and leak tests
					Key ^a	As brazed	Vacuum-exposed, 500 h, 1000°F	Alkali-metal-exposed, 500 h, 1000°F		
Thermalox 998 (99.8 BeO)	Niobium D-43	Zr-19 Nb-6 Be	1940	Potassium ^b	$\bar{x}$	14,343	14,450	14,340	2/2°	Very good results
					s	3,740	250 ^d	490 ^d		
					n	7	2	2		
	Niobium D-43	Ti-48 Zr-4 Be	1940	Potassium ^b	$\bar{x}$	14,130	Not tested	9,710	2/2°	Fair results
					s	4,090		1,940 ^d		
					n	4		2		
Nb-1 Zr		Zr-28 V-16 Ti	2270	Lithium ^e	$\bar{x}$	13,503	12,895	12,000 ^f	4/4°	Good results
					s	2,870	555 ^d			
					n	6	2	1		

All tests on modulus-of-rupture assemblies using Nb-1 Zr metal member.

^aThe symbol $\bar{x}$ = arithmetic mean; s = standard deviation; n = number of specimens tested.

^bOxygen level in associated purity-test capsule was less than 10 ppm.

^cHelium leak rate of less than 1×10^{-9} torr-liter/s.

^dStandard deviation has little significance for sample size of two pieces.

^eAssociated purity-test capsule leaked; no meaningful determination.

^fOne sample only.

Table 15. Corrosion during 1000 h at 1000°C in cesium vapor, cesium reservoir temperature 400°C (Refs. 30, 69)

Material	Origin (type)	Density, g/cm ³	Sample weight, g	Weight change		Comments
				Total, mg	Per surface, mg/cm ²	
Nb-1 Zr	Heraeus		7.0702	+1.4	+0.08	No change in appearance (bright surface).
Tungsten	Plansee		1.6969	+0.2	+0.02	
Tantalum	Heraeus		13.3227	+0.4	+0.01	Bright, weak grain etching.
V-20 Nb-5 Ti	Metallgesellschaft		2.9766	+0.7	+0.05	Rough surface grain etching.
Palladium	Degussa		1.4050	-14.2	-4.6	Formation of large grains, grain etching.
Platinum	Degussa		0.1879	+7.2	+3.6	Slightly discolored at edges.
BeO (>99.5)	CGEC	2.85-2.95	8.8703	-0.8	-0.04	Slightly grey.
Al ₂ O ₃ (Al ₂ O ₃ -0.25 MgO)	Feldmühle (E37)	3.99	10.8926	-2.5	-0.14	Grey.
ZrO ₂	Degussa (Zr 23)	5.4	13.2949	+26.2	+1.4	Slightly grey.
ZrO ₂ (ZrO ₂ -5 CaO HF)	Quarzschnmelze (Thermal ZrO ₂)	4.5-5.1	10.2109	-7.6	-0.5	Grey, partially metalized.
MgO • Al ₂ O ₃	Degussa (Sp 23)	3.3	8.4837	+45.5	+2.6	Black, disintegrated.
MgO	Quarzschnmelze (Thermal MgO)	3.3-3.4	9.0953			Black and grey stains; sample porous.
MgO	Koppers	3.0	7.0992	-36.7	-2.6	

Table 16. Resistance of materials to attack by cesium

Material	Cesium pressure	Temperature, °C			Test time, h	Reference
		Good resistance	Limited resistance	Poor resistance		
Aluminum	10 torr			300-400	1000	70
OFHC Copper	1			900	281	71
	10	300		700	1000	70
Chromium	20	1000			500	72
Cr-23 Al ₂ O ₃	20		1000		1000	72
Cermet						
Gold	1			900	281	71
Ag-50 Cu	1			900	281	71
Hafnium	10 torr	1300			700	70
	4 atm	900			720	71
Iridium	10 torr	1300			500	70, 43
Iron	10 torr	700			1000	43
	20 torr	1000			200	72
	9 atm	1000			450	73
Kovar	10 torr	700			1000	70
Mn-40 Ni	10			300	1000	70
Molybdenum	1	900			281	71
	10 torr	1500			700	70
	1 atm	700			100	74
	9			1000	720	73, 74
	30			1300	100	75
TZM	30 atm			1400	100	52
Nichrome V	10 torr	700			1000	70
Nickel	1 torr	900			231	71
	10 torr	700			1000	70, 43
	1 atm	700			100	74
	9 atm			900	100	74
S P Nickel	20 torr	900			500	72
Nicoro	10			300	1000	70
Microbrazed LM	10	700			1000	70
Microbrazed 170	10	700			1000	43
Niobium	10	700			1000	70
	20 torr	900			500	72
	4 atm	800			720	75
	8	900			720	75
	30			1300	54	75
Nb-1 Zr	4	800			720	75
	8			900	720	75
	30 atm			1300	54	75
FS-82	1 torr			800	280	71
Palladium	10 torr	700			500	70, 43
	20 torr	900			250	72

Table 16 (contd)

Material	Cesium pressure	Temperature, °C			Test time, h	Reference
		Good resistance	Limited resistance	Poor resistance		
Wesgo Al 995 Alumina	10 torr	300		700	1000	70
Silk City SC95D Alumina	10	700			1000	70
Alumina	20			900	300	72
GE A923 Alumina	1			900	24	71
GE A926 Alumina	1	1400			24	71,77
GE A926 Alumina	10	1400			24	77
Alumina-1 Silica	1			1000	24	77
Alumina-1 Silica	100			1000	24	77
Magnesia carborundum 0333	10			300	1000	70
Magnesia carborundum 0340	10	300		700	1000	70
M-H MgO	10		300	700	1000	70
Pd-35 Co	10	700			1000	43
	20	900			500	72
Platinum	1			800	280	71
	10		700		1000	70
	20	900			500	72
Rhenium	10	1200			700	70, 43
Rhodium	10	1200			500	70, 43
Silver	10			300	1000	70
Ag-28 Cu	10		300		1000	70
Ag-1 Ni-30 Cu	10		300		1000	70
304 SS	10 torr	700			1000	70, 43
310 SS	4 atm	800			720	75
321 SS	1 atm		650		100	74
	9 atm			950	100	74
430 SS	1 torr	850			280	71
Tantalum	1.5	1700			100	76
	10	700			1000	70
	20 torr	900			235	72
	4 atm	800			720	75
	8 atm		900		720	75
	30 atm		1300		54	75
Ta-10 W	30 atm		1300		100	72
Titanium	10 torr	300		700	1000	70
Ti-28 Ni	10 torr	300		700	1000	70
Tungsten	10 torr	1200			850	70
	4 atm	800			720	75
	9 atm	900			100	74
	30 atm	1300			100	75

Table 16 (contd)

Material	Cesium pressure	Temperature, °C			Test time, h	Reference
		Good resistance	Limited resistance	Poor resistance		
W-25 Re	30 atm	1300			100	72
Zirconium	10 torr	300		700	1000	70
	4 atm			800	270	75
Quartz	10 torr			300	1000	72
Steatite	10			300	1000	70
Sapphire	10	300			550	
Alsimag	10	300		700	1000	
Feldmühle E37 alumina	10	300		700	1000	
Coors AD 96 alumina	10			300	1000	
Coors AD 99 alumina	10			300	1000	70
Coors AD 995 alumina	10	700			1000	43
	20	900			900	72
Wesgo Al 300 alumina	10	300		700	1000	70
Wesgo Al 400 alumina	10 torr	300		700	1000	70

Table 17. Cesium corrosion test results (Ref. 54)

Test	Atmosphere	Temperature, °C	Time, h	Specimen	Results
49	Cesium	1500	306	Ni brazed Nb to Mo	Leak tight
51		1250	500	Ni brazed Ta to Mo	
52		1250	500	Ni brazed Ta to Mo	
53		1250	500	Ni brazed Ta to Mo metallized alumina	
57		1500	250	Ni brazed Ta to Mo metallized alumina	
64			250	Ni brazed Nb to Mo metallized alumina	Leak tight
73			230	W brazed between W-metallized alumina ceramics	Ceramic cracked
85			230	W metallizing on alumina	No change
86		1500	230	Mo brazed between W-metallized alumina ceramics.	Ceramic cracked
87		1200	500	Same as above	Leak tight
93	Cesium	1200	300	Mo or W brazed between W-metallized alumina ceramics.	Leak tight

A. Beryllia

The microcracking in polycrystalline BeO has been detected by optical and replica electron microscopy and by the following effects that it produces:

- (1) Increase in the open porosity.
- (2) Decrease the $(hk, 0)$ x-ray line broadening.
- (3) Sharp decrease in the modulus-of-rupture.

The irradiation-induced microcracking and eventual powdering depend greatly on the grain size and the irradiation temperature and to a lesser extent on the method of fabrication and the density of the material. This explains the wide range of values obtained by earlier workers for the dose at which powdering starts.

Hickman (Ref. 79) stated that up to about 700°C the onset of microcracking can be related directly to the anisotropic lattice growth as measured by lattice parameter

changes. However, the cause of the microcracking and eventual powdering at temperatures above 700°C has not been definitely established. Microcracking has been observed in specimens irradiated at temperatures $\geq 800^\circ\text{C}$ (Refs. 80 and 81) in which the lattice parameter changes were negligibly small. Possible causes of this microcracking are

- (1) Anisotropic macroscopic growth that is not detected by x-rays, such as that produced by interstitial loops.
- (2) Anisotropic thermal contraction during cooling from the irradiation temperature.
- (3) Intergranular helium bubbles.

Hickman (Ref. 79), by $(hk,0)$ x-ray line-broadening measurements, found that considerable strain relief was produced by subsequent annealing at 1000°C for a few hours in material irradiated at 500° to 700°C. Moreover, Dullow et al. (Ref. 82) and Hickman (Ref. 79) have shown that annealing at 1000° to 1100°C causes complete healing of the microcracks in fine-grain-size material, and recovery of the thermal conductivity and mechanical property changes produced by irradiation. If it is assumed that healing of microcracks occurs during irradiation at 1000°C, the predominant cause of the microcracking observed after irradiations at $\geq 1000^\circ\text{C}$ is probably the strain produced by the anisotropic thermal contraction during cooling from the irradiation temperature. This is consistent with the suggestion by Woollaston and Wilks (Ref. 83) that the strain produced by the anisotropic thermal contraction from 1000°C during fabrication accounts for the microcracking that they observed in unirradiated BeO of 120- μm grain size.

On the basis of his model for the kinetics of irradiation-induced expansion and the assumption that microcracking occurs at a volume expansion of 0.45%, Collins (Ref. 84) predicted the irradiation conditions under which microcracking can be avoided. His estimated combinations of irradiation temperature and neutron flux to avoid microcracking in beryllia of 20- μm grain size and of 2.9-g/cm³ density are shown in Fig. 3. He pointed out the uncertainties in the prediction, which include the annealing behavior of defect clusters and the effect of the helium produced by transmutation. Hickman and Pryor (Ref. 85) used their model for the variation of the damage with irradiation temperature and dose rate and the observation that no microcracking was present in 2- μm material after 7×10^{20} nvt and in 10- μm material after 2×10^{20} nvt for irradiation at 75° to 100°C to deduce the maximum dose that BeO could withstand at a given irradiation temperature without microcracking. Their results, which pre-

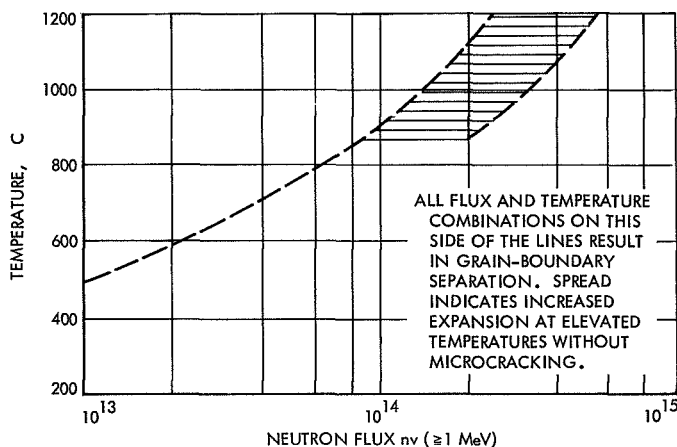


Fig. 3. Estimated minimum irradiation temperature to avoid grain-boundary separation in BeO of 20- μm grain size and 2.9-g/cm³ density (Ref. 84)

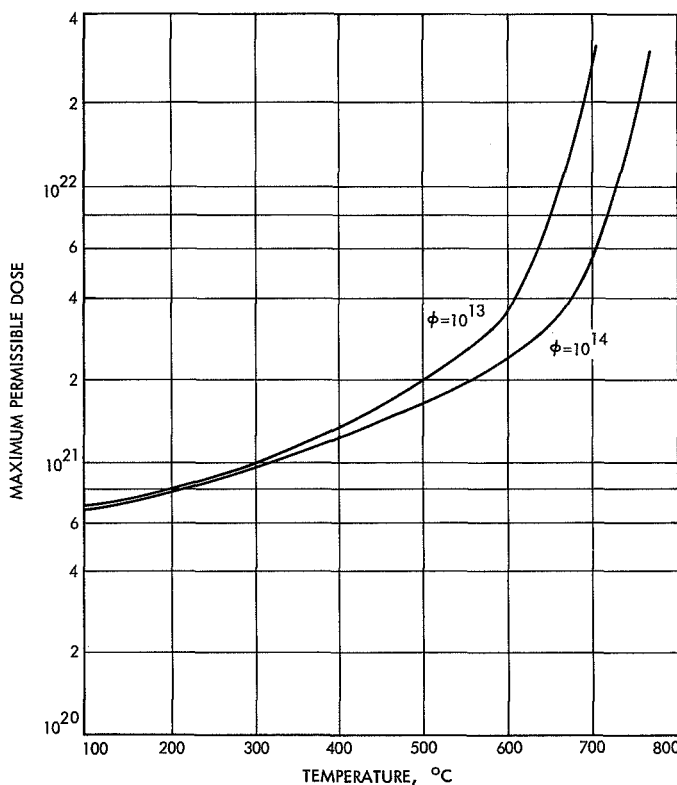


Fig. 4. Maximum dose withstood by polycrystalline BeO, without microcracking, as a function of dose rate and irradiation temperature (Ref. 78)

dict maximum permissible doses of $\approx 1.5 \times 10^{21}$ nvt at 400°C rising to 10^{22} nvt at 700–800°C, are shown in Fig. 4. However, the observations used for this prediction are not reproducible, and for nominally identical material Hanna et al. (Ref. 86) and Hickman et al. (Ref. 79) have found

more recently that the onset of microcracking occurred at doses two or three times less than those observed by Hickman et al. Moreover, Hickman et al. have pointed out that this model underestimates the damage at temperatures above 700°C, and that the curves should have a smaller upward curvature at these temperatures.

B. Alumina

No irradiation-induced microcracking was observed by optical microscopy in polycrystalline alumina irradiated at $\approx 80^\circ\text{C}$ to doses in the range 5×10^{19} to 5×10^{20} nvt (Refs. 87 and 88). However, Higgins (Ref. 89) claimed that microcracking was visible by x-ray microscopy in material of 50- μm grain size and 0.5% porosity, after irradiation at 150°C to doses of 3.2×10^{19} and 1.3×10^{20} nvt, respectively. He concluded that microcracking depended upon a high porosity and that the cracks nucleated at pores within grains.

Thorne and Howard (Ref. 90) reported that no cracking was visible in polycrystalline specimens of 5% to 30% porosity irradiated to doses up to 1.1×10^{21} nvt at 250° and 475°C , respectively. However, both extruded (31% porosity) and slip-cast (25% porosity) material disintegrated after doses less than 1.4×10^{20} nvt at 700°C , whereas sintered material (8% porosity) irradiated to a dose of 5.6×10^{20} nvt at 700°C showed no evidence of cracking until further irradiated to a dose of 10^{21} nvt. They suggested that the cracking resulted from microcracks that were caused by irradiation effects or thermal effects, or both.

C. Magnesia

The irradiation-induced growth of magnesia has been determined by density measurements of Hickman and Walker (Ref. 91) and by measurements of linear dimen-

sions of Desport and Smith (Ref. 92). Irradiation-induced changes in the density of polycrystalline material have been determined by Hickman and Walker (Ref. 91) and by Stevanovic and Elston (Ref. 87). The dimensional changes have been converted into density changes and are shown with the results of the density measurements in Fig. 5; the data are for irradiations at $\approx 100^\circ\text{C}$ except where other temperatures are shown. The results of Hickman and Walker (Refs. 91 and 93) differ greatly from those of Desport and Smith. For comparable doses, the density change decreases with increasing irradiation temperature.

The recovery of the linear dimensions (Ref. 92), and of the density (Ref. 91) on subsequent isochronal (1-h) annealing usually, for a given annealing temperature, drops as dose or irradiation temperature rises.

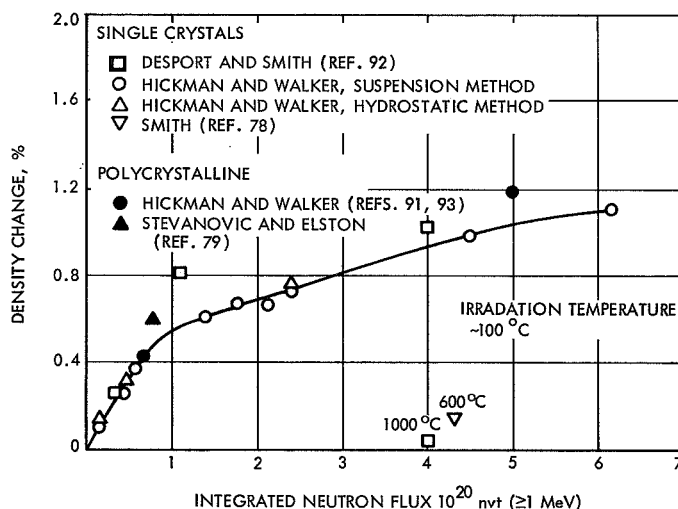


Fig. 5. Effect of neutron dose and irradiation temperature on the macroscopic density of MgO (Ref. 78)

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