

Second Quarterly Report
for
Study of the State-of-the-Art of the Hermetic Seals
for Secondary Alkaline Spacecraft Cells
(20 Sept. 1967 - 20 Dec. 1967)

Contract No.: NAS5-10432

Prepared by

R. F. Fogle

W. R. Scott

for

Goddard Space Flight Center
Greenbelt, Maryland

Second Quarterly Report
for
Study of the State-of-the-Art of Hermetic Seals
for Secondary Alkaline Spacecraft Cells
(20 Sept. 1967 - 20 Dec. 1967)

Contract No.: NAS5-10432

Goddard Space Flight Center

Contracting Officer: A. L. Essex
Technical Monitor: Eugene Stroup

Prepared by

TRW Systems Inc.
One Space Park
Redondo Beach, Calif.

for

Goddard Space Flight Center
Greenbelt, Maryland

TABLE OF CONTENTS

	Page
SUMMARY	i
INTRODUCTION	1
1. DISCUSSION	1
1.1 Analysis of Seal Types and Manufacturing Methods Now in Commercial Use	1
1.1.1 Glass-to-Metal Seals	2
1.1.2 Ceramic-to-Metal Seals	3
1.1.3 Glass Ceramic Combinations-to-Metal	4
1.1.4 Rigid Plastic-to-Metal	4
1.1.5 Elastomer-to-Metal	4
1.1.6 Synthetic Polymeric (Non-Elastomer) Material-to-Metal Seal	5
1.2 Evaluation of Seals and Sealing Techniques Not Now in Commercial Use	5
1.3 Cell User, Test Organization and Manufacturer Contacts	7
2. PROGRAM FOR NEXT REPORTING PERIOD	8
3. CONCLUSIONS	8

TABLES

		Page
Table I	Summary of Hermetic Seal Types Used Commercially	9, 10 & 11
Table II	Some Properties of Materials Commonly Used in Glass-to-Metal and Ceramic- to-Metal Seals	12 & 13
Table III	Summary of Hermetic Seals Not in Commercial Use	14 & 15
Table IV	List of Cell Vendors and Users Visited During Program	16

SUMMARY

The following Progress Report is submitted in accordance with NASA Contract NAS5-10432 Study of the State-of-the-Art of Hermetic Seals for Secondary Spacecraft Cells.

Phase I of the program, consisting essentially of a conceptual analysis of seal types and manufacturing methods is complete. This phase included a literature survey of manufacturing methods for various types of hermetic seals with emphasis on the integrity of seals, applications, and limitations. At the conclusion of the program, after all data has been analyzed, an attempt will be made to evaluate the life expectancy of the various type seals.

Phase II "secondary spacecraft cell user and test organization contacts" has been completed. Three trips were made during the months of October, November and December. The users visited were 1) Bell Laboratories, Murry Hill, N.J.; 2) U. S. Naval Research Laboratories, Washington, D.C.; 3) The Boeing Company, Seattle, Wash.; 4) Lockheed Sunnyvale, Calif.; 5) APL Laboratories, Johns Hopkins University, Silversprings, Md.; 6) General Electric Space Center, Valley Forge, Pa.; 6) RCA Space Center, Princeton, N.J.; 7) U.S. Naval Ammunition Depot, Crane, Ind.

Phase III "contacts with secondary spacecraft cell manufacturers" has been completed. Also, several companies supplying seals to the cell manufacturers were visited. The cell manufacturers visited were 1) Texas Instruments, Attleboro, Mass. (not presently engaged in the manufacture of spacecraft cells); 2) Sonotone Corporation, Elmsford, N.Y.; 3) Gulton Industries, Metuchen, N.J.; 4) Ceramaseal, Inc., New Lebanon Center, N.Y. (manufacture of ceramic-to-metal seal for General Electric space cells); 5) General Electric, Schenectady, N.Y. (presently engaged in testing a new design ceramic-to-metal seal for spacecraft cells).

An analysis of the data and information obtained from the various users and manufacturers has been started. Although detailed analysis has not been completed, it is evident from the questionnaires and personal visits that there is no standard method for testing for the hermeticity and integrity of hermetic seals used for spacecraft cells and thus correlation of data will be difficult.

INTRODUCTION

This report presents the progress made on a study to determine the state-of-the art of hermetic seals for secondary alkaline spacecraft cells. One factor which can limit the life of spacecraft cells, especially for long duration missions (3 years and longer), is the hermetic seal. TRW was awarded a contract by NASA-Goddard to do a study of the state-of-the-art of these hermetic seals. The program was broken down into (1) a conceptual analysis of all types of hermetic seals, (2) user and test organization contacts to determine their experience with hermetic seals used in secondary spacecraft cells to discover problem areas, (3) vendor contacts to determine manufacturing methods used in seal production, the quality control and test performed to insure the quality of the seal, (4) evaluation of future seals and sealing techniques not presently flown in spacecraft cells, (5) evaluation of information collected and recommendations.

The conceptual analysis, user and test organization contacts, and cell manufacturer contacts phases are complete. The evaluation of new seals and analysis of information collected during visits has been initiated.

1. DISCUSSION

1.1 ANALYSIS OF SEAL TYPES AND MANUFACTURING METHODS NOW IN COMMERCIAL USE. The following discussion relates to all type seals which have or are presently manufactured commercially. Some but not all of the seals presented have been used on secondary alkaline spacecraft cells. Some of the characteristics, limitations, advantages, cost and manufacturing processes of each type seal are presented.

In general, an ideal hermetic seal for spacecraft cells should 1) be unaffected by the internal atmosphere of the cell, 2) be unaffected by potential gradients resulting from charge and discharge, 3) be unaffected by other cell components or products resulting from degradation of these components 4) be able to retain its integrity over a wide pressure range, 5) be able to retain its integrity over a considerable temperature range, 6) lend itself to ease of manufacture with no crucial steps, 7) lend itself to ease of inspection, 8) be relatively low in cost and 9) have and maintain structural integrity. If all the above conditions are achieved, spacecraft cells could be built with low cost, long life hermetic seals. Unfortunately, present day seal technology is not capable of meeting all nine requirements listed above. However, the technology has developed to a stage where seals are capable of wide temperature and pressure variations with no degradation to the seal, provided good process control is maintained. Also, it is reasoned that products resulting from degradation of cell components other than the seal itself, would have little effect on the seal compared to the caustic

atmosphere of the cell electrolyte solution. Thus, in this report, the evaluation of various seal types during the conceptual analysis phase was directed toward 1) effect of internal cell atmosphere on seal, 2) effect of potential gradients on seal, 3) effect of manufacturing process on seal, and 4) relative seal cost.

Table I summarizes the various type seals that have seen commercial application. As was mentioned in the First Quarterly Report, and as evidenced by Table I, most of the commercially manufactured hermetic seals were developed for applications in the electronic industry. Recent development of seals capable of withstanding extreme conditions of temperature (excess of 1000°C) and attack by alkali metal vapors resulted from research programs on thermionic conversion. The next section presents a detailed analysis of the various type seals manufactured commercially.

1.1.1 GLASS-TO-METAL SEALS. The two types of glass-to-metal seals presented in Table I (matched and unmatched) were introduced in the First Quarterly Report. The main advantages of these type seals are their low cost, wide choice of glass-metal combinations and their ease of manufacture. Table II shows some properties of glasses and metals used for glass-to-metal seals. The technology of glass-to-metal sealing techniques and manufacturing methods is highly developed, more so than any other type of hermetic seal, and results in a very reliable product for the usual applications.

The main disadvantage for both types of glass-to-metal seals presented in Table I is that all glasses are attacked by caustic (KOH) solutions. Some glasses are more resistant than others but all show some degree of corrosion by caustic solution. Thus, to insure long life of glass-to-metal seals, the glass must be protected from direct contact with the electrolyte.

Although various coating materials have been applied to glass-to-metal seals used in alkaline battery cells, they have all been unsatisfactory in that the bond is weak and with time the coating material separates exposing the glass.

Another disadvantage of the glass-to-metal seal is difference in thermal expansions at the glass-metal interface resulting in cracks. The chemical attack can also be accelerated at the glass-metal interface because of the stresses resulting from the differences in thermal expansion. For space application, cracking and accelerated chemical attack at the glass-metal interface would result in leaking cells. One other disadvantage of the glass-to-metal seal is the mechanical weakness of the bulk glass phase to mechanical shock.

Development of a reliable coating material to protect the glass from attack by the caustic electrolyte solution in alkaline spacecraft cells, and proper design to off-set the mechanical weakness of the bulk glass phase would result in acceptable long life seals.

1.1.2 CERAMIC-TO-METAL SEALS. As with the glass-to-metal seals, a preliminary discussion of the ceramic-to-metal seals presently manufactured was presented in the First Quarterly Report. An expanded discussion is presented here. The ceramic-to-metal seals being mass produced use either the sintered metal powder, (e.g., moly manganese) or active metal manufacturing process. The two processes produce seals having higher mechanical strength and higher temperature limit than the glass-to-metal seal. The active metal process is more critical than the refractory metal powder process because the parts have to be assembled prior to firing and purity of materials is more important. Also, there is less versatility in the selection of materials for the active metal process. Although the manufacturing process for the active metal type seal is more critical and the selection of material is less than for the refractory metal powder process, it is the only one currently used for seals of spacecraft cells. Table II shows the properties of some materials commonly used in ceramic-to-metal seals. The main disadvantages of the metal-to-ceramic seals manufactured by the above two processes, when incorporated in cells, is silver migration and leakage. Most braze materials presently used in seals are silver-copper alloys. Under the influence of the potential gradients across the ceramic insulator of the seal, and the contact of the seal with caustic electrolyte solution, the silver of the braze slowly migrates across the ceramic resulting ultimately in a shorted cell. An electrodeposit of nickel or some other type (epoxy) protective coating over the silver braze material is being used to reduce this migration, but for long duration missions, the possibility still exists. Gold, nickel and other type braze materials are being developed in hopes of eliminating this problem, but no long-term testing of these seals in cells has been realized, and thus their reliability for such applications has not been established.

Cracks in the ceramic itself and cracks developing at the ceramic-metal interface which would result in leaks for spacecraft application, are primarily a result of poor quality control of the manufacturing process. In the active metal process, too much titanium hydride can result in a brittle area in the braze which can develop fissures when the seal is temperature cycled. Also, if the alignment of the mating parts is poor resulting in different braze thicknesses, temperature cycling can induce uneven stresses causing small fissures at the metal-ceramic interface. Cracks in the ceramic itself are probably a result of poor incoming inspection of purchased ceramic parts and poor inspection of manufactured parts. As mentioned earlier, good quality control procedures can greatly reduce cracks in the ceramic and ceramic-metal interface, thus reducing the probability of leaks in spacecraft cells.

Another disadvantage of the metal-to-ceramic seals is that they are higher in cost than glass-to-metal seal and are not suited to mass production techniques.

- 1.1.3 GLASS CERAMIC COMBINATIONS-TO-METAL. Two types of glass ceramic combinations-to-metal seals are currently manufactured. One uses a high glass content ceramic which bonds to metal when brought to temperature. The seal is a glass-to-metal type and has most of the disadvantages of the regular glass-to-metal seal. It is a low temperature seal subject to attack of caustic solutions. It does have a slightly better structural stability than regular glass-to-metal seals in that the bulk ceramic-glass phase is mechanically stronger than glass alone. This seal is relatively low in cost, but not widely used. In the other type of glass ceramic combination seal, glass frit or glass-metal frit is incorporated as an intermediate layer between the ceramic and metal. More dimensional control is available with this seal than the high glass content ceramic seal. This seal again has most of the disadvantages associated with regular glass-to-metal seals. It is widely used for low temperature metallizing and solder seal assemblies. These combination type seals do not present any distinct advantages over regular glass-to-metal seals and incorporate most of their disadvantages.
- 1.1.4 RIGID PLASTIC-TO-METAL. In this type seal, the rigid plastic is bonded to the metal by an adhesive. In one type, an acetonitrile/styrene copolymer plastic is bonded to the metal using epoxy adhesives. The seal is made by casting the sealant around metal. This type seal is produced commercially at low cost in a one step process. This type seal is mechanically weak, subject to chemical attack, and temperature limited. This type seal has been used on silver-cadmium space cells with some degree of success. However, the mechanical weakness of this type seal make it a poor risk as a seal for long duration missions. The long-term chemical stability of these type seals in contact with KOH has yet to be demonstrated.
- 1.1.5 ELASTOMER-TO-METAL. In this type seal, rubber-like insulating materials are bonded to metal parts under compression to form a hybrid (bonded-compression) type seal. Usually a combination chemical process (vulcanizing) and heat are used to effect a bond between the elastomer and metal. The seal is designed to keep the elastomer under compression at all times. This type seal is mechanically weak in comparison to metal-to-ceramic seals, and is temperature limited. However, elastomers can be chosen on basis of their chemical resistance for each application. The seal is relatively cheap and easily produced. Several attempts at using this type seal for spacecraft cells has been unsatisfactory. The seal failure apparently results from a breakdown of the bond between the elastomer and the metal resulting in leaky cells.

1.1.6 SYNTHETIC POLYMERIC (NON-ELASTOMER) MATERIAL-TO-METAL SEAL. This type seal is also a hybrid type seal. The seal is effected by both bonding and/or compression. Polymeric materials such as teflon, Kel-F, nylon, etc. are bonded to the metal parts under compression. The seal design is such that the polymeric material is kept under compression. Although selection of polymeric materials to resist chemical attack is possible, this type of seal is unsatisfactory in that large seal area is required, poor bonding characteristics are realized, high degree of compression is required to maintain seal, and the polymeric materials are subject to cold flow and stress crazing problems. These type seals have been used for alkaline secondary cells on a commercial basis where life and hermeticity requirements are not as severe as space requirements.

1.2 EVALUATION OF SEALS AND SEALING TECHNIQUES NOT NOW IN COMMERCIAL USE. The seals presented in this section are not produced on a commercial basis, but they have potential application for spacecraft cells. Table III presents a summary of these various type seals, mostly ceramic-to-metal. Most of the sealing techniques presented in Table III are in the development stage, or have been developed but have not been produced in quantity. The fact that most of the seals presented in Table III are in the development stage, or would possibly require some development of manufacturing techniques would place the initial cost of these seals considerably above those presently employed for hermetically sealing spacecraft cells.

As can be seen from the data in Table III, most of the ceramic-to-metal seals depend on a final brazing operation to effect the final seal, and therefore these seals would be subject to the same problems associated with the ceramic-to-metal presently used. Although no performance data was obtained for these seals, their justification for development was probably based on cost reduction, ease of manufacture, specific application, etc. Undoubtedly their development was also based on some need or requirement in the electronic industry.

Two of the ceramic-to-metal seals presented in Table III do not depend on brazing as such to effect the final seal. One of these is a direct fusion of the ceramic to the metal. The direct fusion is a welding process accomplished by the use of a high intensity, focused beam of electrons. The method has been successful for spot welds, such as tab welding to micromodule substrates, but welds larger than spot welds are susceptible to massive cracking. If indeed, larger area welds are realized, this method would have promise for space cells because it would eliminate the problems (dendritic migration) associated with the braze alloys used in today's ceramic-to-metal seals. The other type metal-to-ceramic seal presented in Table III which does not necessarily require a conventional braze to effect the final seal is the ceramic

brazing technique. This technique was developed for metal-to-ceramic seals capable of withstanding temperatures in excess of 1200°C. In this method, the ceramic is fused to the metal member by melting a suitable oxide eutectic between mating parts. In one high temperature seal of this type, the ceramic is first metallized using either a suspension of WO_3 (tungsten oxide), or MoO_3 (molybdenum oxide), then a mixture of RuO_2 (ruthenium oxide) and MoO_3 is melted between the metallized ceramic and molybdenum in a hydrogen atmosphere. The RuO_2 and MoO_3 decompose and the Ru and Mo melt, wet, and flow into the metallized layer and braze to the refractory molybdenum metal. These type seals are in research and development stages. Their cost, even after development, would be quite high but they do eliminate the conventional braze materials which have been troublesome.

Another type seal presented in Table III is the devitrified glass seal. In this method, a conventional glass-to-metal seal is made, then by heat treatment (time-temperature) the glass is converted into a devitrified ceramic. The devitrification process can be varied to obtain ceramics having very different properties. If a devitrification process could be developed which would result in a devitrified ceramic which was stable in an atmosphere that is present within cells, and had the desired electrical and mechanical properties, it should provide a long life seal for space cells.

The graded cermet-to-metal of Table III is in concept an ideal seal in that it would also eliminate the problems associated with conventional glass-to-metal and ceramic-to-metal seals. In the manufacture of this seal, successive layers of metal powder gradually enriched with ceramic powder are bonded together with heat and pressure to provide a seal between pure metal and pure ceramic sections. These type seals are in the experimental stage, and the cost would be expected to be very high due to the development required. Also, these seals are subject to a considerable amount of internal stresses.

The compression seal presented in Table III is strictly a compression type employing no adhesives to effect the seal. The seal is known as a Zigler seal, named after its inventor, and has been patented (Patent No. 3,109,055). The seal is composed of an internally threaded sleeve that is disposed about an externally threaded insulating bushing which is provided with an axial bore through which a conducting rod extends. The seal is effected by circumferentially deforming the sleeve along a portion of its length to radially compress the sleeve about the bushing and the bushing about the conductor. This type seal is not subject to the normal problems associated with glass-to-metal and ceramic-to-metal seals, but could be troubled with cold flow and possibly radiation problems.

The seal, once tooling is set up, could be manufactured rapidly at low cost and with a high degree of reproducibility. Some experimental cells utilizing this type seal have been on a continuous overcharge at the C/10 ratio and room ambient temperatures for five years with no seal failures or apparent degradation. In the experimental seal, the insulation bushing was Kel-F and it has shown no signs of cold flow. This type seal shows promise for long-term spacecraft application and warrants further evaluation.

1.3

CELL USER, TEST ORGANIZATION AND MANUFACTURER CONTACTS.

Phase II, "User and Test Organization Contacts", and Phase III, Manufacturer Contacts has been completed. Questionnaires were sent out to selected users, test, organizations and manufacturers. A tabulation of the results of these questionnaires was presented in the First Quarterly Report. Those organizations not responding to the questionnaire were contacted by telephone, and most indicated their experience was not related to the study. All organizations responding to questionnaires who indicated a personal visit by program representative would be beneficial to the study program were contacted by telephone and arrangements were made for visitations. The various organizations were visited during the months of October, November and December. The various organizations visited and personnel contacted are listed in Table IV.

The manufacturers were questioned regarding 1) manufacturing process, quality control and test methods used to determine integrity of seal, 2) effect of stresses induced by welding cover to case, 3) what dendritic problems were associated with the seal and what, if any, measures were being taken to eliminate problems, 4) how seal was designed to reduce mechanical stresses, 5) new seal designs and sealing techniques. Also, test data and procedures were obtained if not considered company proprietary information.

Users and test organizations were questioned regarding 1) methods used for testing the integrity of seal, 2) quality control measures imposed on vendors, 3) inspection procedures used in-house for checking for leaking cells, 4) types of seals used, 5) problems encountered such as leaking seals, and dendritic problems associated with seal, 6) whether seal should be fitted with one or two insulated seals, 7) whether threaded or soldered lugs are more desirable for space cells.

As mentioned in the First Quarterly Report, the questionnaire returned by the user and test organizations indicated that tests performed throughout the industry for determining the integrity of the hermetic seal were not uniform. The visits confirmed that there is no uniformity of test methods, and that even for a given test method, there is a considerable variance in procedure.

At present, the information and data obtained from the visits is being compiled and evaluated. The complete analysis of this data will be presented in the final report.

2. PROGRAM FOR NEXT REPORTING PERIOD. The program for the remainder of the contract will include the compilation and analysis of information and data received from the various users, test organizations and cell manufacturers. After the data has been analyzed, a report will be prepared which will summarize the current state-of-the-art of hermetic seals and will include recommendations appropriate to establishing guidelines for future seal research and development.
3. CONCLUSIONS. Conclusions made at this point in the program are tentative and will be subject to review in the final report.

It is apparent from both the questionnaire responses and direct discussions with users, test organizations and manufacturers that there is no uniformity of the methods and procedures used for testing the integrity of hermetic seals (leak test especially). In addition, no universally accepted test methods appear to be available.

The conceptual analysis of commercially used hermetic seals showed that these seals are not capable of meeting all the requirements for long life space cells. Some attempts to adapt commercially manufactured hermetic seals to meet the rigid requirements for space cells have been unsuccessful and others are in the evaluation stage, but at present, no hermetic seal has the capability required for space cell application.

Some of the hermetic seals not presently manufactured on a commercial scale (seals in research and development stage) show promise for space cell application. Those seals, such as the Zigler seal and the devitrified glass seal, that show promise for space cell application, do so because they eliminate or greatly reduce the problems (chemical attack, silver migration) associated with the type of seals presently used.

SUMMARY OF HERMETIC SEAL TYPE

TYPE OF SEAL	SUB TYPE	CHARACTERISTICS	TYPICAL MATERIALS	FABRICATION PROCESS
1. Glass-to-Metal	a) Matched Seals	Expansion coefficients of materials are matched to withstand stresses.	<ol style="list-style-type: none"> 1. Kovar, moly. or tungsten with hard glass (borosilicates). 2. Iron or nickel alloys with soft glass (lead). 	<ol style="list-style-type: none"> 1. Chemical cleaning. 2. Oxidize metal parts. 3. Glass applied in plastic state under slight pressure. 4. Metal oxides dissolve in glass. 5. Etch and plate metal parts.
	b) Unmatched Seals	Thermal expansion coefficients not matched, metal ring designed to hold glass in compression	Iron, Low carbon steel or stainless steel with soft or hard glass	Similar to process for matched seals although oxidation not required
2. Ceramic to Metal	a) Sintered Metal Powder seals (refractory metals)	Strong, high temp. seals with a variety of metal parts available for brazing to ceramic parts	Kovar, Mo, Cu, Ni, monel or stainless steel parts, high alumina ceramics with Mo or W based metallizing powders, silver brazing alloys (other alloys used also)	Metal powder in lacquer applied to ceramic and fired at 1300 - 1500° C in controlled atmosphere so metal oxide reacts with ceramic to form bond. Metallizing is electroplated and brazed to metal parts

INHERENT ADVANTAGES INHERENT LIMITATIONS PRODUCIBILITY COST FACTOR APPLICATIONS EXPERIENCE

1. Seal design flexibility due to matched expansion characteristics.	Low resistance to attack by alkali solns. Metals subject to corrosion. Low radiation resistance.	Mass produced on a commercial basis for electronic field - various sizes available	Relative low cost	Electronic devices (diodes and transistors), electrical feed throughs
2. Hermeticity.				
3. Inspectable seals.				

Wider selection of metals than for matched seals	Lower resistance to attack by alkali solns. Hermeticity restricted to a lower temp. than matched seals. Low radiation resistance	Same as for 1 a	Low cost	Same as for 1 a
--	--	-----------------	----------	-----------------

No critically sensitive variables to process, withstand high temp. and thermal shock, excellent dielectric properties, hermeticity, radiation resistant, non-magnetic metal powders	Silver migration from brazing alloy possible, and no way to inspect for this phenomena	Produced on a commercial scale. Most widely used seal in industry today	More costly than glass counterparts	Same as 1 a although not as widely used. Used extensively for power electron tube enclosures. Used in spacecraft cells.
---	--	---	-------------------------------------	---

SUMMARY OF HERMETIC SEAL TYPES

TYPE OF SEAL	SUB TYPE	CHARACTERISTICS	TYPICAL MATERIALS	FABRICATION PROCESS
2. Ceramic to Metal (Cont.)	b) Active Alloy Seals	Same as 2 a with less selection of materials	Kovar or moly metal parts, high alumina ceramics, metallizing with Ti or Zr hydrides or metal powders, silver or nickel transition brazing metals	Process requires that all parts and materials be assembled in position during a one shot vac. firing operation. At high temp. materials in contact react to form a strong chemical bond
3. Glass Ceramic combinations to metal	a) Glass Ceramic combination	Combines a mixture of glass and ceramic to obtain a low temp. seal	Various metals, ceramics and glasses	Ceramic has high glass content which bonds to metal when brought to temp. Forms glass to metal type seal
	b) Glass Coated Ceramic	Ceramic insulator is coated with glass or glass-metal frit to obtain low temp. seal	Same as 3 a plus glass frit. Also a variety of metal-glass frits are used	Intermediate layer of glass frit or glaze is incorporated between ceramic and metal to form seal. Fabrication in H ₂ eliminates chemical cleaning.
4. Rigid Plastic-to-metal		Metal terminals are bonded to plastic with adhesives	Acrylonitrile/styrene copolymer plastic, (Union carbide bakelite C-11 molding cpd.), Epoxy adhesives, plated metal terminals	Seal is made by casting sealant around metal terminal

ES USED COMMERCIALY

INHERENT ADVANTAGES INHERENT LIMITATIONS PRODUCIBILITY COST FACTOR APPLICATIONS EXPERIENCE

Same as 2 a except more critically sensitive to processing variables	Seal fabrication processes are critical (assembly and purity of materials), silver migration from brazing alloy possible	Used on a commercial basis	Normally more costly than sintered metal powder seals	Used on power electron tube enclosures
Permits fabrication of complex assemblies with wide selection of materials. Relatively low temp. sealing process for ceramic parts	Expansion characteristics not matched, limit on temp. range and chemical resistance	Limited use	Less than 2 a, low cost ceramic seals	Not widely used
Same as 3 a above, dimensional control	Same as 3 a	Used commercially	Less than 2 a, low cost ceramic seals	Widely used for low temp. metallizing and solder sealed assemblies
Uses commercially available materials, low cost, no close tolerances required, one step operation	Mechanically weak, limited chemical resistance, long term hermeticity questionable, temp. limited, pressure limited, poor reproducibility	Produced on a commercial basis	Low cost	Used on alkaline battery cells, evaluated for space craft cells, no leakage problems

SUMMARY OF HERMETIC SEAL TY

TYPE OF SEAL	SUB TYPE	CHARACTERISTICS	TYPICAL MATERIALS	FABRICATION PROCESS
5. Elastomer-to metal		Rubber-like insulating materials are bonded to metal parts under compression to form a hybrid bonded-compression type seal	Various selected metals, various elastomers selected on basis of chem. resistance and other properties required (butyl, ethylene propylene, chlorosulfonate)	Combination chemical process (Vulcanization and heat used to bond elastomer to metal. Seal design forms a mechanical compression that keeps elastomer under compression
6. Synthetic Polymeric Material-to-metal seal		Mechanical compression type of seal similar to 5 except insulating material is not elastic	Various metals, Polymeric materials such as Teflon, Kel-F, nylon (reinforced with fiberglass, adhesive bondable	Seal design

USES USED COMMERCIALY

	INHERENT ADVANTAGES	INHERENT LIMITATIONS	PRODUCIBILITY	COST FACTOR	APPLICATIONS EXPERIENCE
1 g) nd ion r	Same as 4, no critical processing and steps required	Same as 4 except reproducibility is relatively good, loss of elasticity	Readily producible	Low cost	Can be used for a variety of applications, have been tested on spacecraft cells
	Polymeric materials can be selected for specific properties required such as chemical resistance, strength etc.	Large seal area req'd., temp. limited. Poor bonding characteristics (Teflon and Kel-F) high degree of compression req'd. to maintain seal, cold flow and stress crazing problems	Readily producible although may be complex design	Requires molding and machining, relatively expensive compared to 4 and 5	Used in alkaline cells where life and hermeticity requirements are not severe

TABLE II
SOME PROPERTIES OF MATERIALS COMMONLY USED IN GLASS-TO-METAL AND CERAMIC-TO-METAL SEALS

Material	Linear Coeff. Of Thermal Expansion Per $^{\circ}\text{C} \times 10^{-6}$ (25 - 300 $^{\circ}\text{C}$)	* Melting Point ($^{\circ}\text{C}$)	Magnetic Attraction	Corrosion Resistance	Remarks
<u>Metals</u>					
Molybdenum	5.5	2625	None	Poor	Hard glass seals
Nickel-Iron Alloys (Kovar)	5.0	1450	Strong	Fair	Low electrical and thermal conductivity, hard glass and ceramic seals
Tantalum	6.7	2995	None	Poor	Hard glass seals
Stainless Steel (Ni-cr-Fe)	18.2	1400	Little	Good	Ceramic Seals
Nickel	14.6	1450	Strong	Excellent	Ceramic Seals
Cold Roll Steel (SAE 1010)	13.5	1450	Strong	Poor	Soft glass seals
Monel (Ni-Cu)	15.0	1350	Little	Excellent	Ceramic Seals
Copper	16.4	1083	None	Fair	All seals
Chrome Iron	9.0	1400	-	Fair	Soft glass seals

*

The temperatures given in the melting point column are 1) the melting point temperature for metals, 2) the safe operating temperature for the ceramics, and 3) the softening point temperature for glasses.

TABLE II (Cont'd.)
 SOME PROPERTIES OF MATERIALS COMMONLY USED IN GLASS-TO-METAL AND CERAMIC-TO-METAL SEALS

Material	Linear Coeff. Of Thermal Expansion Per $^{\circ}\text{C} \times 10^{-6}$ (25 - 300 $^{\circ}\text{C}$)	* Melting Point ($^{\circ}\text{C}$)	Corrosion		Remarks
			Magnetic Attraction	Resistance	
<u>Ceramics</u>					
Alumina (Al_2O_3)	6.5	1700	-	Excellent	Not attacked by alkali solutions
Steatite ($\text{MgO}\cdot\text{SiO}_2$)	6.9	1000	-	Good	Not attacked by alkali solutions
Forsterite ($2\text{MgO}\cdot\text{SiO}_2$)	10.0	1000	-	Good	Not attacked by alkali solutions
Zircon ($\text{ZrO}_2\cdot\text{SiO}_2$)	4.4	1100	-	Good	Not attacked by alkali solutions
<u>Glasses</u>					
Soft Glasses (Soda-Lime and Lead Glasses)	9.0	620	-	Poor	Slow corrosion in alkali solutions
Hard Glasses (Borosilicates)	4.6	700	-	Fair	More resistant to chemical attack than soft glasses

* The temperatures given in the melting point column are 1) the melting point temperature for metals, 2) the safe operating temperature for the ceramics, and 3) the softening point temperature for glasses.

TYPE OF SEAL	CHARACTERISTICS	FABRICATION PROCESS	INHERENT ADVANTAGE
1. Ceramic-to-Metal	Direct fusion of ceramic-to-metal	Ceramic and metal parts are fused together directly under high intensity focused beam of electrons	Variety of metal ceramics can be joined by this process
2. Ceramic-to-Metal	Ceramic brazing	The ceramic is fused to metal member by melting suitable oxide eutectic between mating parts	For use in joints must withstand to above 1200°C
3. Glass-to-Metal	Devitrification of glass to form ceramic-to-metal type seal	Joints are made by conventional glass-to-metal manufacturing methods, then by heat treatment (time-temp.) The glass is converted to a devitrified ceramic	Conventional glass metal manufacturing processes utilize Physical, electrical and chemical processes could be varied wide range
4. Metal-to-Ceramic	Refractory-Metal salt coating	Ceramic immersed in soln. of refractory metal salt, dried, fired to reduce metal salt, electroplated, then brazed by conventional methods	Can be used to make inside diameters holes
5. Metal-to-Ceramic	Refractory-metal-Oxide Coating	Similar to refractory-metal powder process except metal is applied as oxide instead of in elemental form	Lower sintering temperature

TABLE III

SEALS NOT IN COMMERCIAL USE

PROCESSES	INHERENT LIMITATIONS	COST FACTOR	APPLICATIONS EXPERIENCE
s and process	Welds larger than spot welds are susceptible to massive cracking	No cost data available	Tab welding to micromodule sub- strates has been shown to be feasible
which amp.	-	-	Research and development stage
ss-to- ing ed. ical, properties over a	Possibly the control of devitrification process (time-temp. relationship) would require rigid control to obtain de- sired properties	Cost could be expected to be much lower than conventional ceramic-to-metal seals	No known commercial use of process in this country
metallize of	Areas not to be metallized would have to be masked	No cost data available	Developed and used for ceramic-metal tube programs
	Same as for the refractory-metal- powder process	No cost data available	Developmental stage

SUMMARY OF HERMETIC SEALS NO

TYPE OF SEAL	CHARACTERISTICS	FABRICATION PROCESS	INHERENT ADVANTAGES
6. Metal-to-Ceramic	Condensed vapor coating	A thin metallic coating applied by volatilization of a metal and its deposition onto the ceramic, followed by brazing or electroplating and then brazing	Variety of ceramic and metal can be used, equipment necessary relatively inexpensive, no excessive heating of ceramic, metallized ceramics produced rapidly
7. Graded Cermet-to-Metal	Mixture of ceramic and metal powders are bonded together in varying proportions ranging from pure ceramic to pure metal	Successive layers of metal powder gradually enriched with ceramic powder are bonded together with heat and pressure to provide a seal between essentially pure metal and pure ceramic sections	Wide selection of materials, permits design to specific desired characteristics
8. Synthetic Polymeric Material-to-Metal	Compression type seal with Kel-F	Compression of metal tube about polymeric material through which extends a metal conductor	Ease of fabrication, no braze problem, materials relatively stable chemically, reproducibility

nt'd.)

T IN COMMERCIAL USE

INHERENT LIMITATIONS

COST FACTOR

APPLICATIONS EXPERIENCE

Bond between ceramic and metal is a mechanical instead of a chemical bond and is weaker than chemical bond

Relatively low cost

No commercial applications

Limited physical designs must be compatible with process

Very high due to development required

No commercial application to-date. Special high temp. for corrosive environment produced at Westinghouse

Possible cold flow, crazing and radiation damage of polymeric materials, temperature limitation, size limitation

Low cost after initial tooling cost

No known commercial application