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CERAMIC-TO-METAL SEAL TECHNOLOGY (U). / R.H. BRISTOW GENERAL ELECTRIC, SCHENECTADY, NY JAN 66

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Ceramic-To-Metal Seal Technology

R. H. Bristow

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TECHNICAL INFORMATION SERIES

R66ETI-2
JANUARY 1966

CERAMIC-TO-METAL SEAL TECHNOLOGY

by

R. H. Bristow

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AUTHOR R H Bristow	SUBJECT	NO R66ETI-2
		DATE Jan 1966
TITLE Ceramic-to-Metal Seal Technology		O.E. CLASS 1
		GOVT. CLASS None
REPRODUCIBLE COPY FILED AT MICROWAVE TUBE BUSINESS SECTION TUBE DEPARTMENT SCENECTADY, NEW YORK		NO. PAGES 44
SUMMARY <p>This paper formed the basis for a lecture on metallic-nonmetallic seals, presented in April 1964 to a course in "The Science and Technology of Modern Ceramics", which met at the M&P Laboratory, Schenectady, N.Y.</p> <p>This course, comprising a series of twelve lectures, was conceived and coordinated by Dr. D. S. St. Pierre of the General Electric Research Laboratory, and was sponsored jointly by the American Society for Metals and the Central New York Section of the American Ceramic Society.</p>		
KEY WORDS		

INFORMATION PREPARED FOR**TESTS MADE BY****AUTHOR** R. H. Bristow**COMPONENT** Microwave Tube Operation, Tube Department**APPROVED** R. J. Bondley

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INTRODUCTION

The major applications for glass-to-metal and ceramic-to-metal seals are found in the electrical industry where such seals serve the dual purpose of electrically isolating yet "hermetically" sealing various portions of a device. The term "hermetic", although widely used, is not yet capable of precise definition (ASTM Committee F-1, Sub-Committee V, is currently studying the problems of measuring and classifying leak rates in metallic-nonmetallic seals). In some applications, such as electrical feed-throughs for capacitors and transformers, a seal is merely required to be liquid or oil tight. In many more applications, such as lamps, vacuum and gas-filled electron tubes, space simulation chambers, etc., a seal must be gas-tight or, as this condition is more commonly referred to, vacuum tight. A vacuum-tight seal is generally considered to be one which, when tested on a helium-peaked mass spectrometer leak detector, shows a leakage rate of less than 10^{-10} cc of air per second. It is this latter type of seal with which this report is primarily concerned.

Although glass-to-metal seals serve admirably in many applications, there is a continually growing usage of ceramic-to-metal seals. Ceramic-to-metal seals possess a number of advantages and very few disadvantages when compared with their glass counterpart:

Advantages

1. Higher mechanical strength and generally better thermal shock resistance
2. Lower dielectric loss, particularly at elevated temperatures
3. High volume resistivity and freedom from electrolysis effects
4. Tolerant of higher processing and operating temperatures
5. Better corrosion resistance
6. Nuclear radiation resistant.

Disadvantages

1. Not transparent to visible radiation (except for costly sapphire-to-metal seals)
2. Residual stresses cannot be precisely determined nor relieved by heat treatment
3. Cost is often higher than a similar-function glass-to-metal seal.

It was the attainment of the first four advantages that spurred several German investigators to develop methods for sealing ceramics to metal in the early 1940's. The application for such seals was electron tubes -- tubes which could operate at higher frequencies and with improved ratings. It is significant to note that most advances which have been made in the technology of ceramic-to-metal sealing during the past twenty years have occurred as a direct result of the needs of the growing electron tube industry. Consequently, extensive reference will be made to the electron tube throughout this paper - in tracing the historical development of ceramic-to-metal sealing, and in discussing seal designs and materials of construction.

Until the introduction of ceramic materials to tube construction, designs were based upon extensive use of glass as insulation for electrical conductors, as portions of the vacuum envelope, and for exhaust tubulations. For further information on the many materials and the now well established techniques of glass-to-metal sealing, the reader is referred to the several excellent books and papers treating of this subject in considerable detail.^{1-8*}

This paper will be concerned solely with ceramic-to-metal sealing and will consider the techniques by which ceramics and metals can be joined, the seal designs which are most often used, and the materials of construction employed therein. An attempt will be made to acquaint the reader with the most successful of the various systems of materials which are available to the designer of devices requiring hermetic seals.

Most ceramic-to-metal seals utilize an impervious, polyphase ceramic from the group steatite, forsterite, alumina and beryllia. By far the major interest has been, and continues to be, in seals to the so-called high alumina ceramics; ceramics containing from 85 to nearly 100 per cent aluminum oxide. Later we will examine the reasons for this choice, as

* A bibliography appears on page 41

well as some of the problems which it has generated. Although relatively little use has yet been made of devitrified glass-ceramics in seals,⁹ a tremendous amount of effort is currently going into research and development of such materials. This relatively new engineering material is melted and formed as a glass and is subsequently subjected to a heat treatment which nucleates and grows crystals (devitrification) in the glass. Because of the small size of the crystals which are formed, the extent of crystallization which can be achieved, and the completely pore-free structure of the material, devitrified glass-ceramics can be made to have very high mechanical strengths. Since the thermal expansion can be controlled through the composition and quantity of the crystalline species which form, materials can be "tailored" to the expansion of useful metals. Thus, it is to be expected that this class of materials will find rapidly increasing application in metallic-nonmetallic sealing.

JOINING TECHNIQUES

BASIC APPROACHES

There have been so many methods and materials employed to join ceramics to metals that it is difficult to properly categorize them. In order to facilitate discussion, however, we can list five basic approaches to the problem:

1. Inorganic and organic adhesives
2. Mechanical and pressure-diffusion seals
3. Noble-metal coatings
4. Refractory-metal metallizing
5. Active-alloy sealing.

In addition, we will consider several new techniques which are being developed to meet the recent need for ceramic-to-metal seals capable of long life in severe environments.

1. INORGANIC AND ORGANIC ADHESIVES

The most important technique to be found under this heading is the use of glass as a cementing medium. Since glasses can be made to adhere to properly oxidized metals, and since glasses will readily wet and bond with the surface of most ceramics, we find a convenient (and one of the first) methods for cementing metals to ceramics. This system of materials, however, possesses several limitations: (a) the processing and operating temperature of a sealed component is limited by the softening temperature of the glass; (b) a very close match of the thermal expansion characteristics of the three members is required; (c) the mechanical strength and thermal shock resistance are limited by the presence of a glassy bond; and (d) the preparation of a seal often requires manipulation by an experienced glass worker. In spite of these disadvantages, seals of this type have been and are still used in certain tube constructions; for example, in mercury-containing ignitrons and tank rectifiers. It is the presence of mercury which

dictates the use of glass as the bonding medium, since mercury reacts with and is contaminated by most of the brazing alloys employed in other ceramic-to-metal sealing systems.

During recent years there has been considerable interest in the use of high-temperature glasses and partially crystalline "ceramic adhesives" for ceramic-to-metal as well as metal-to-metal joining. For example, several airframe manufacturers have investigated the use of such adhesives for the sealing of alumina radomes to their supporting hardware. Although these efforts have not been entirely successful, the work is continuing and the knowledge gained may some day be useful in developing new or improved seals for electronic devices.

Although many organic adhesives are useful for joining metals to ceramics, they suffer the common limitations of low operating temperature capability (250°C maximum), high vapor pressure, and high thermal expansion. Nevertheless, epoxy and silicone resins have found limited application as sealants in electronic devices and, as their properties are improved, they will undoubtedly find wider acceptance. It should also be noted that Glyptal* and anerobic permafil (although not used as the primary seal) have saved-the-day for many an experimenter and tube manufacturer alike, by plugging an elusive leak in a ceramic-to-metal seal of a costly device or system.

2. MECHANICAL SEALS

As the name indicates, such seals are those in which the metal member is held in intimate contact with the ceramic by mechanical means and the bond, if there is one, is mechanical rather than chemical in nature.

A recent patent¹⁰ detailed the construction of an electron tube wherein metal members having ductile "knife edges" machined therein were held in intimate contact with the ends of a ceramic cylinder by means of a bolt through the center of the tube. The bolt acted as a strain storage element and it was possible to heat the tube to moderate temperatures before the pressure applied to the seal was lost. The vacuum tightness of such seals is due to plastic deformation of the ductile metal "knife edges" to provide intimate contact with the ceramic member. Such seals are vacuum tight only so long as adequate pressure is maintained at the interface.

A similarity will be noticed between such seals and those which are effected in the demountable metal flanges of vacuum systems wherein a copper, gold or aluminum gasket is plastically deformed into intimate contact with the stress concentrating ridges or grooves of mating flanges. The flanges,

*Registered trademark of General Electric Company

however, are made from the same metal and thus have identical thermal expansion behavior. In the case of mechanical ceramic-to-metal seals, the materials ordinarily do not have similar expansion characteristics and the design of a seal which will remain vacuum tight during thermal cycling is made much more difficult.

Within the past few years, another method¹¹ has been quite successfully employed to effect mechanical seals to alumina ceramics. Basically, the method involves pressing a copper-plated steel cylinder onto the tapered end of a high-strength alumina ceramic. Plastic flow of the ductile plating effects a vacuum-tight joint and, if the interface is maintained under sufficiently high radial pressure, the seal is capable of being thermally cycled to moderate temperatures. The materials must be carefully selected in order to permit the maintenance of a high hoop stress in the metal cylinder (for high-temperature capability) without generating a radial force so high as to cause fracture of the ceramic.

If selected metals and ceramics are forced into intimate contact at elevated temperatures in a protective atmosphere, interdiffusion and reaction will take place and the result will be a vacuum-tight pressure-diffusion seal¹². Copper was found to bond well to a steatite ceramic after one hour at a temperature of 1000°C in an atmosphere of nitrogen under a pressure of several thousand pounds per square inch. The limitations of such seals are many, however, and they have not found commercial application.

Diffusion bonding to an adherent metallic layer previously applied to the surface of a ceramic has met with somewhat greater success and applicability. In one method, diffusion bonding of the abutting surfaces of copper washers and copper-plated metallized ceramic rings was employed in the assembly of miniature ceramic receiving tubes¹³. Another application for diffusion bonding is the joining of gold foil to a gold-plated, thin molybdenum layer applied to the periphery of a fused silica disk to form a vacuum-tight microwave window.

3. NOBLE-METAL COATINGS

One of the oldest techniques for applying a metallic layer to a ceramic or glass article involves the use of a solution (metallo-organic compound) or dispersion of a precious metal in a suitable vehicle (usually with added ceramic-type fluxes) which is painted on the surface of the article and fired to a temperature sufficient to develop a bond. Paints made from gold, silver, palladium, platinum, rhodium and iridium have been used.

Noble-metal coatings are familiar as decorations on glass and ceramic articles, as conducting paths in ceramic printed circuits, and as metallic surfaces on ceramics to which other components can be attached by soft soldering. Since such coatings are generally quite thin, they are usually built up by electrodeposition of copper prior to soldering, in order to prevent stripping of the coating from the surface of the ceramic. Brazing (hard soldering) is generally not possible because of the solubility of the noble metal in the brazing alloy, resulting in loss of adherence of the coating.

Although noble-metal coatings have found wide application in electronic components, the more adherent, refractory-metal-type coatings permit greater latitude in the selection of soldering or brazing alloys.

4. REFRACTORY-METAL METALLIZING PROCESSES

We now come to what the writer prefers to call refractory-metal metallizing processes but which, in addition to the refractory metals of tungsten and molybdenum, includes iron, nickel, cobalt and chromium. The first three materials are the most important, however, and are the basis of the widely used molybdenum-manganese technique and modifications thereof. It will be enlightening to briefly trace the development of this process.

Extensive studies by German investigators prior to World War II were directed toward the elimination of glass (which had been used to bond metal-to-ceramic parts in their ceramic tube development programs) through the application of a powdered metal to the surface of the ceramic, followed by sintering at a high temperature. It was desired that the resulting sintered metal layer be firmly adherent to the ceramic and be amenable to brazing by hard solders.

Vatter¹⁴ described the application of a layer of powdered iron to a ceramic followed by sintering in vacuum at 1250°C. In a later patent¹⁵ he expanded this technique to include nickel, chromium, molybdenum, or tungsten intimately mixed with 0.5 to 10.0 percent by weight of one or more of the oxides, hydroxides, or carbonates of calcium, titanium, barium, manganese, zirconium, thorium, and silicon.

Pulfrich¹⁶ is credited with both the first commercial production of ceramic vacuum tubes and the development of the molybdenum metallizing process. According to this invention, a refractory-metal powder is spread on a steatite-type ceramic containing a "mineralizer" followed by sintering at a temperature approaching the softening point of the ceramic. It is claimed that a low melting eutectic in the ceramic wets the molybdenum particles and that, on cooling, this liquid crystallizes so that the metal

particles are anchored not in a glass flux but in the crystal structure of the ceramic. Mineralizers which he mentioned included pyrolusite (MnO_2); the oxides of barium, calcium, or zirconium; and sodium tungstate.

Hunt¹⁷ and Gross¹⁸ described the technique as used at Telefunken for the production of metal-ceramic radio tubes. The latter report included details of the production of tubes by Dr. Pulfrich's molybdenum technique and indicated that, in practice, two percent of iron powder was added to the molybdenum metallizing mix and that about two mils of nickel was sintered onto the molybdenum coating prior to brazing.

Nolte¹⁹ found that the incorporation of manganese in a molybdenum-based coating promoted reaction with the ceramic surface and the formation of an improved bond. This "moly-manganese" metallizing method²⁰ and modifications thereof^{21, 22} are now the most widely used methods for sealing to ceramics.

Indeed, there have been many modifications in composition and processing as each user sought to make the process simpler or more reliable. Although the metallizing of steatite and forsterite ceramics, at a temperature about 100°C below their original maturing temperature (1250°C to 1350°C), presented few problems (using for example, an 80 w/o Mo, 20 w/o Mn metallizing composition), vacuum-tube manufacturers encountered difficulty in attempting to use the same process for metallizing the high-alumina ceramics (greater than 94-percent alumina) which were rapidly becoming available in the early 1950's. High-alumina ceramics are polyphase, predominately crystalline materials consisting of alpha alumina crystals (and small amounts of secondary crystalline phases) bonded by a refractory, alkaline-earth aluminosilicate glass. For metallizing a 94-percent alumina ceramic with a mixture of 80 w/o molybdenum, 20 w/o manganese, it was found that a metallizing sintering temperature of 1500 - 1600°C was required to form a tightly adherent, vacuum-tight coating. This same procedure, however, was not necessarily effective when metallizing an alumina ceramic containing 96-percent or more aluminum oxide. Thus, the search was on for reliable methods for metallizing these very refractory, low glass content ceramics which possessed the very desirable attributes of low dielectric loss at ultra-high frequencies and high temperatures, excellent mechanical strength and good heat shock resistance.

In these early years of the ceramic-enveloped tube, many government-funded tube development programs included tasks directed toward the attainment of vacuum-tight ceramic-to-metal seals. It was soon recognized, however, that a lack of understanding existed as to the fundamental mechanisms of ceramic-metal bonding and that recurring problems could be expected

until some of the art of ceramic-to-metal sealing was replaced by science. Since many manufacturers were using molybdenum-based metallizing processes, primary interest centered around the physical and chemical interactions which occurred when a molybdenum metallizing coating was sintered to the surface of a ceramic, as well as the interrelationship of metallizing composition, ceramic composition, and sintering conditions. Although several contracts were awarded to investigate the metallizing process, they contributed little beyond that which had been provided by the excellent pioneering work of Pincus^{23,24}. Successful techniques for metallizing most ceramics of interest to the tube manufacturer have since been empirically developed; however, the desire for more fundamental understanding still persists. At the present time, several industry and government sponsored research programs^{25,26,27} are seeking this information, making use of newer analytical techniques such as the x-ray microprobe.

Let us look a little deeper into the problem of metallizing of ceramics and examine some of the structures which can be obtained. Basically, we want to apply a dense, predominately metallic coating in such a manner that it will be tightly adherent and vacuum tight. If one applies powdered molybdenum to the surface of a pure alumina ceramic or sapphire and heats to a very high temperature in a nonoxidizing atmosphere, no significant bond will be developed since there is no appreciable reaction between these materials below the melting point of alumina. If, however, the same pure molybdenum coating were to be applied to one of the so-called high-alumina ceramics, say a 94-percent alumina type (balance SiO_2 , MgO , CaO), and heated to about 1550°C , some bonding would be obtained. Microscopic examination of a polished section would show a sintered but quite porous molybdenum layer which had become attached to the ceramic by virtue of a penetration of the glass phase (a viscous liquid at the metallizing temperature) of the ceramic into the pores of the molybdenum coating. The extent to which the glass phase penetrates the molybdenum coating depends largely upon its viscosity (and, therefore, composition), the porosity of the molybdenum layer, and the furnace atmosphere. Even at this temperature, which is so high as to allow warpage of the ceramic, the pores of the molybdenum coating may not be completely filled if it is more than a few tenths of a mil thick. Thus, unless the brazing material can be induced to fill these pores, a vacuum-tight joint will not be obtained.

Now, if manganese is added to this molybdenum paint, reactions occur at lower temperatures. However, to function as a bond-promoting agent the manganese must first be oxidized to MnO . This is achieved, during sintering, by maintaining sufficient moisture in the hydrogen sintering atmosphere

as to drive the reaction in that direction. Failure to maintain a slightly oxidizing atmosphere will result in volatilization of manganese since the vapor pressure of elemental manganese is quite high at the temperatures of interest (1 Torr at 1250°C, 20 Torr at 1500°C). Thus, when this molybdenum-manganese mixture is applied to the surface of a 94-percent alumina ceramic and heated to 1500°C, the MnO which is formed reacts with the crystalline (Al_2O_3 , MgAl_2O_4) and glassy (SiO_2 , MgO, CaO) phases present in the ceramic at the interface, forming a liquid which can more easily penetrate the pores of the molybdenum layer. Depending upon the exact temperature, manganese aluminate crystals may form at the sintering temperature or will form during cooling. Thus, the sintered molybdenum layer will be attached to the ceramic by means of a partly glassy, partly crystalline "reaction product" which interpenetrates the molybdenum coating and the ceramic.

Before examining further the interrelationship of metallizing composition and ceramic composition, let us consider the problem of porosity in the metallizing coating. Since molybdenum is not readily wet by the commonly used hard solders (silver, silver-copper, gold-copper), it is desirable to apply a thin layer of nickel and/or copper, by electrodeposition or reduction from the oxide, to enhance flow of the braze over the surface. If the molybdenum layer is thin or the pores are large and interconnected, the electroplating and braze metal will be able to penetrate and seal off all channels through the coating and a vacuum tight seal will result. If, however, the coating is very thick or the pores are small, the braze will penetrate only a short distance leaving a region in the center of the molybdenum coating through which gas can leak.

If the liquid oxide "reaction product" can be induced to penetrate, and be retained in, the pores of the sintered molybdenum coating, then the braze need only wet and bond to the surface of this coating in order to effect a vacuum-tight joint. However, if the reaction product is too plentiful or too fluid, it may cover the surface with an oxide or glassy film which would inhibit electroplating. Thus, it can be seen that all of the parameters mentioned must be carefully controlled in order to achieve consistently high quality coatings. It is little wonder that many of the early tube development programs met with difficulty in preparing vacuum-tight seals.

Still another consideration is that the sintered metallizing must be predominately metallic, but must not be so dense that the mechanical adherence provided by the penetration of the ceramic-like reaction product into the pores of the molybdenum coating is lost. For example, sintering of a

molybdenum-based metallizing coating typically produces a molybdenum "sponge" which is interpenetrated by the reaction product or interfacial layer which is formed (Figure 2). However, if one percent nickel powder is added, and the coating is sintered at the same temperature, the molybdenum particles sinter into completely dense, pore-free patches or plates. Since there is little opportunity for mechanical interlocking of the interface material with the molybdenum, the strength of adherence of this coating to the ceramic is less than one-third that of the one without the nickel additive. Thus, it can be seen that mechanical interlocking plays a very important role in determining the strength of adhesion of a metallizing coating.

Mention was previously made of the difficulty of metallizing very high alumina content ceramics with metallizing compositions which had been used successfully on forsterite and the less refractory alumina ceramics. Basically, the difficulty resulted from failure to form a sufficient quantity of a liquid phase having the proper viscosity at the sintering temperature to penetrate and be retained in the sintered molybdenum layer. It is the near absence of a glass phase in the ceramic with its liquid-promoting, viscosity-controlling oxides SiO_2 , CaO , and MgO which causes poor bonding. One solution to the problem has been to add, to the metallizing composition, some of the oxides which are lacking in the ceramic. Some of the additives which have been reported to enhance bonding of the basic molybdenum-manganese composition include silica, magnesia, calcia, kaolin, talc, titanium in the form of metal, hydride and oxide, zirconium hydride, ground steatite ceramic and many others.

One might question the wisdom of adding glass-forming oxides to the coating in apparent contradiction of Pulfrich's¹⁶ recommendations to form coatings in which "the metal particles are anchored not in a glass flux, but in the crystal structure of the ceramic". In actuality, if the additives are carefully chosen and properly proportioned, the reaction product at the interface consists of crystals bonded by a glassy matrix - the same structure which exists in the base ceramic. This fine-crystal structure can be seen in the coating of Figure 1-A, a coating containing liquid-forming additives which was sintered at the relatively low temperature of 1300°C .

The coating of Figure 1-B contained only molybdenum and manganese - no oxide additions - and was sintered at 1500°C . The similarity in structure can be seen.

Although such coatings are quite satisfactory, it is often preferred to achieve a structure as shown in Figure 2 in which the corundum grains at

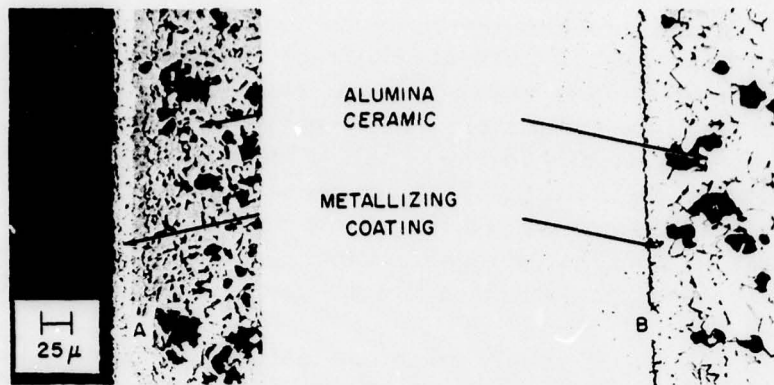


Figure 1 - Molybdenum-Manganese Metallizing Coatings on Alumina Showing the Crystalline Structure of the Interfacial Region: (a) Coating Containing Oxide Additions; (b) No Oxide Additions

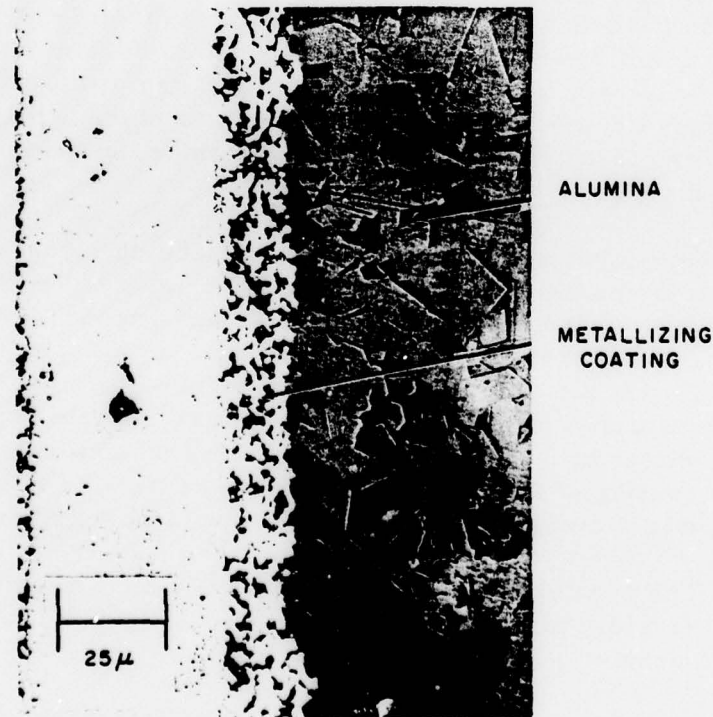


Figure 2 - Molybdenum Metallizing on Alumina Showing Interpenetration of Corundum Grains with the Coating at the Interface

the interface have grown out into the molybdenum layer, firmly locking it to the substrate. In this case, the reaction product serves to fill the interstices of the coating and occurs only as isolated pockets at the interface.

Many other factors affect the results obtained -- the particle size of the refractory-metal powder^{28, 29}, the grain size of the alumina ceramic^{30, 31}, the oxygen content of the sintering atmosphere²⁷ and the bulk density of the unfired coating to mention but a few. For further discussion of these and other parameters, the reader is referred to the references listed.

Other methods for applying refractory metal coatings to ceramics include vapor deposition and plasma arc spraying. The resulting coatings usually lack the adherence and density so necessary for effecting vacuum tight ceramic-to-metal seals and have thus far not found commercial application.

Still another method for applying a coating of molybdenum to ceramic involves the decomposition of a molybdenum compound and/or reduction of the oxide. Molybdenum trioxide, upon reduction in hydrogen, yields extremely fine particles of molybdenum which form a more adherent coating than would be obtained had the molybdenum been applied in elemental form. Furthermore, some of the oxide melts (M. P. -795°C) before it can be reduced to metal, the oxide liquid reacting vigorously with the oxides of the ceramic. Molybdenum trioxide can be conveniently applied as a suspension in an organic vehicle or it can be dissolved in ammonium hydroxide and applied as a true solution. Lithium, calcium and barium molybdates can be used in a similar manner, and the alkali and alkaline earth metal oxides which are liberated upon decomposition assist in the formation of a strong bond by acting as a flux for the ceramic.

5. ACTIVE-ALLOY SEALING PROCESSES

If two perfectly smooth surfaces are brought into intimate contact, they will adhere. A rather crude example of this phenomenon is found in the sticking which occurs when polished steel gauge blocks are placed together. However, surfaces having the degree of smoothness necessary for developing a truly strong bond are not ordinarily obtained and, as the surface roughness increases, the interfacial contact required for the formation of a strong joint decreases. If, however, a liquid is introduced which wets the surface of the solid, excellent interfacial contact is restored. An analogy here is the thin film of spilled coffee which wets both the cup and the saucer, causing them to stick together.

In a ceramic-to-metal joint, factors such as mechanical keying and chemical reaction at the interface influence the strength of the bond which is produced, however, interfacial contact is a prerequisite to the development of any adherence. Consequently, in sealing metals to ceramics we are initially concerned with methods of promoting interfacial contact between a rigid metal member and a brittle ceramic.

In the several sealing processes which are most widely used in industry, this is achieved through the use of a third material -- a solder or braze metal. The liquid braze material wets the surface of both the metal and the ceramic and, upon solidification, a strong vacuum-tight joint is formed. Although we now have a means for filling the gap which exists between the rough surfaces of the metal and the ceramic, we have yet to see how the metal braze can be made to wet the surface of a dissimilar material -- ceramic.

Basically, there are two methods for accomplishing this: (1) by providing an adherent metallic surface (a metallized coating) on the ceramic which will be readily wet by a brazing alloy, as has been discussed in the previous section, and (2) by making additions (such as titanium) to the molten braze that will cause it to wet the oxide ceramic.

The wetting and spreading characteristics of liquids on solid surfaces are often studied by the sessile drop method. In this method measurements are made on a drop of liquid resting at equilibrium on a solid surface, the shape of the drop being determined by interfacial and gravitational forces. From these measurement, the surface tension and contact angle can be calculated.³²

Figure 3 shows a drop of liquid in contact with a solid having a resultant contact angle θ (the angle between the solid surface and the tangent to the liquid surface at the contact point). Relationships between the liquid-vapor surface energy (γ_{LV}), the solid-vapor surface energy (γ_{SV}), and the solid-liquid interface energy (γ_{SL}) are given by the equation of Figure 3. If the solid-liquid interface energy is high, the liquid tends to form a spherical drop having a small interface area. On the other hand, if the solid-vapor interface energy is high, the liquid will tend to spread out and eliminate this interface. The contact angle may vary between $\theta = 180^\circ$, and $\theta = 90^\circ$ is considered to be the boundary between nonwetting ($\theta > 90^\circ$) and wetting ($\theta < 90^\circ$).

Oxide liquids have much lower surface energies than solid metals and consequently oxide liquids tend to wet metals on which they are placed. In contrast, liquid metals have much higher surface energies than most ceramic oxides and the interface energy is high, with the result that pure liquid metals do not wet and spread on ceramic surfaces. Wetting can be induced, however, if an addition can be made to the liquid metal which will reduce the interface energy.

Figure 4 shows the rapid decrease in interfacial energy which results from the addition of titanium to molten nickel in contact with a single-crystal alumina surface.³³ This lowering of interfacial energy results from preferential adsorption of the more electropositive component at the liquid-solid interface. This selective adsorption causes a marked change in interfacial energy to occur over a narrow concentration range of the solute element -- this is believed to be caused by the formation of a monolayer of the adsorbed ion at the interface. In this work, the selective adsorption of titanium was confirmed by x-ray fluorescence analysis of the metal-ceramic interface and x-ray diffraction confirmed the predicted presence of the reaction compound Ti_2O_3 .

The development and use of active alloy sealing techniques long preceded the wetting studies which have supplied a partial understanding of the underlying phenomena. In the early 1940's, F. C. Kelley³⁴ made important observations concerning the wetting of nonmetallic materials by copper-titanium alloys. R. J. Bondley³⁵ successfully applied these phenomena in his development of the very useful titanium-hydride sealing process. In this process, the areas of the ceramic to which a seal is desired are painted with a suspension of titanium hydride in a suitable vehicle. The metal and ceramic parts are then assembled with rings or washers of a soft solder or a brazing alloy (usually lead, silver-copper eutectic or gold-copper alloys) in contact with the hydride. Upon heating, the hydride dissociates leaving a residue of pure titanium on the surface of the ceramic. When the melting temperature of the brazing alloy is reached, it will spread over all surfaces which have been coated with hydride and the resulting alloy will wet and bond to the surface of the ceramic. After dissociation of the hydride at temperatures above about $600^{\circ}C$ the pure, finely divided elemental titanium is an extremely active getter for oxygen and water vapor, both of which will impair its ability to impart ceramic wetting qualities to the braze metal. Although it has been found easiest to maintain a low oxygen-content atmosphere (in spite of possible outgassing of the parts being brazed) by performing the operation in vacuum, successful sealing can be accomplished in pure inert gases or extremely dry hydrogen.

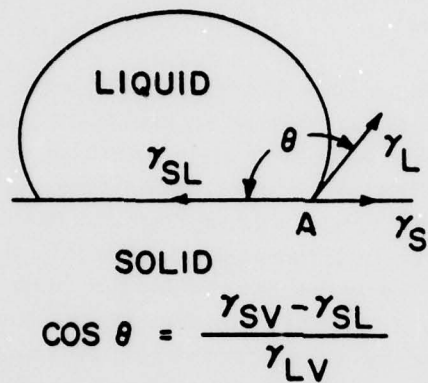


Figure 3 - Sessile Drop and Interfacial Energy Relationships

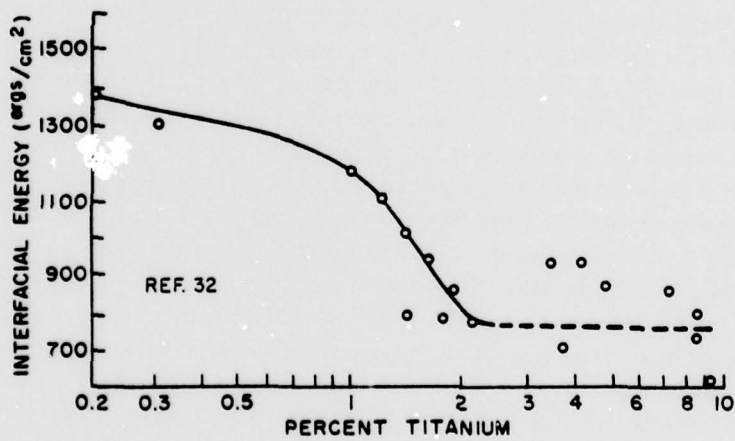


Figure 4 - Effect of Titanium Additions on the Interfacial Energy of Molten Nickel on Sapphire

Pearsall and Zingesser³⁶ made an extensive study of active-alloy sealing techniques and reported that in addition to titanium hydride, they successfully used the hydrides of zirconium, tantalum and niobium for brazing to ceramics and other inorganic materials. It was found that the operation could be carried out in vacuum or in atmospheres of highly purified hydrogen, helium, argon and nitrogen. These investigators also prepared vacuum-melted alloys of active metals, particularly titanium and zirconium, with silver, copper, silver-copper eutectic and aluminum; such alloys showing good wetting and bonding to ceramics. They also experimented with thin sheets of active metal and brazing alloys placed together in contact with the ceramic and heated to the alloying temperature, as well as metal powder mixtures used in the same manner.

Another variation of the active-metal technique was introduced by a manufacturer by brazing alloys.³⁷ The heart of the technique is a silver-copper eutectic alloy wire having a core of elemental titanium which comprises about 5 to 8 percent by weight. A ring of this wire is assembled with the metal and ceramic parts to be brazed and the assembly is heated in vacuum or other oxygen-free protective atmosphere. The silver-copper eutectic alloy sheath melts at 778°C and at a slightly higher temperature the melt alloys with the titanium core to form the reactive alloy. Seal design is very important in order to prevent the eutectic melt from running out of the joint before it has had an opportunity to alloy with the titanium core. Although wire consisting of a homogeneous alloy of titanium in the silver-copper eutectic composition would be more useful, its manufacture has not been possible.

Another very reliable technique of active-alloy sealing was contributed by J. E. Beggs.³⁸ Beggs employed titanium metal as the structural and electrical conducting components of his vacuum devices and a specially developed matching ceramic for the insulating members. They were sealed together by interposing a thin shim or foil washer of nickel or copper and heating to the eutectic temperature: 942°C in the case of nickel and 875°C in the case of copper. The titanium-containing eutectic alloy wets and bonds to the ceramic in much the same manner as occurs in the titanium-hydride technique. Seals of this type are generally made in vacuum although they can also be made in an inert atmosphere.

It is merely necessary that the liquid which is formed at the sealing temperature contain a small percentage of titanium -- it makes no difference whether the titanium be contributed by the structural parts or the foil washers. Thus, titanium foil can be used to form eutectic bonding liquids at the interface between metals such as copper, nickel, iron, Kovar, and stainless steel

and ceramics such as forsterite, alumina, spinel, magnesia, zirconia, and many others. In addition, ceramics can be sealed to other ceramics as well as to refractory metals by using washers of both titanium and a eutectic-forming metal such as copper or nickel in the proper proportions. When designing a seal, due consideration must, of course, be given to the thermal expansion mismatch which exists between many of the above mentioned materials.

The presence of brittle intermetallic compounds in most of these binary titanium systems necessitates precautions to minimize their occurrence in a seal.³⁹ Figure 5 shows the equilibrium diagram for the system titanium-nickel. It will be recognized that when a thin shim of nickel is placed between titanium and a ceramic member and heated to 942°C, the first liquid to form will have the eutectic composition. If the seal is immediately cooled to room temperature, the interface will be found to contain a large amount of the brittle intermetallic compound Ti_2Ni . If heating is continued above the eutectic temperature, the composition of the liquid in equilibrium with the solid will become richer in titanium, and if held at a temperature above the eutectic, the liquid would gradually disappear due to diffusion of nickel into the massive titanium member. The time-temperature treatment which yields the highest quality seals lies between these two extremes.

If multiple shims of titanium and nickel are used to seal alumina-to-alumina or alumina-to-tantalum, for example, the phase composition of the solidified alloy will be predictable from the composition which is selected. If the shims are proportioned to give the eutectic composition, as in the seal of Figure 6-A, the alloy at room temperature will contain a large amount of Ti_2Ni . Many fine cracks therein will constitute a leak path through the seal. If the shims are proportioned so as to yield an alloy richer in titanium (83.2 w/o Ti, 16.8 w/o Ni) the seal will contain less of the intermetallic, as in Figure 6-B. The most satisfactory way of eliminating Ti_2Ni in such seals, however, is to use a "buffer" washer of titanium. That is, a washer sufficiently thick (0.005-inch to 0.010-inch) that it will never be completely alloyed by the thin nickel foil on either side, thus, making the seal one of titanium-to-ceramic on one side of the buffer washer and titanium-to-refractory metal on the other side, as shown in Figure 7.

In light of this sensitivity of seal quality to the presence of Ti_2Ni , one might logically ask how it is possible to make a satisfactory seal of alumina-to-nickel,⁴⁰ using a titanium-foil washer. Indeed, if such an assembly is subjected to the same time-temperature treatment as is normally given seals to titanium, it would contain a very high percentage of Ti_2Ni at the

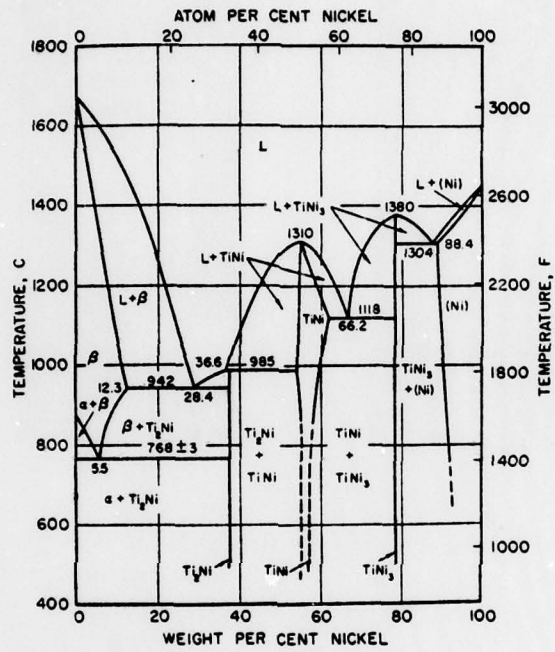


Figure 5 - Titanium-Nickel Equilibrium Diagram

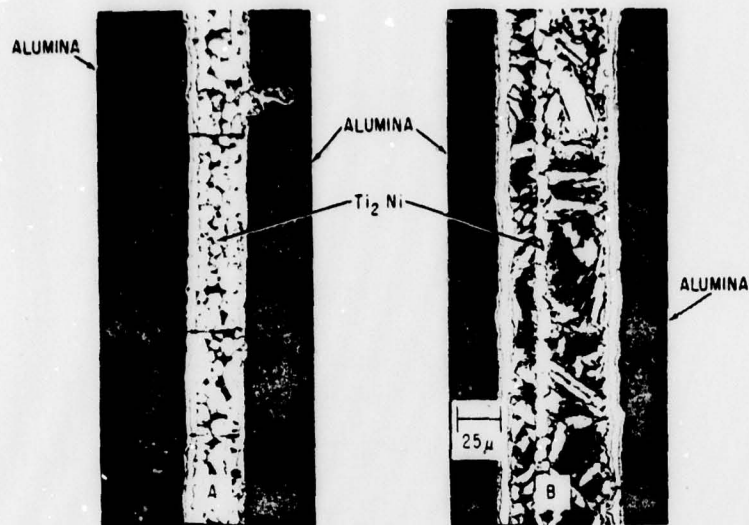


Figure 6 - Titanium-Nickel Shim Seals of Alumina-to-Alumina Prepared with Alloy Compositions: (a) 78 w/o Ti, 28 w/o Ni; (b) 83.2 w/o Ti, 16.8 Ni

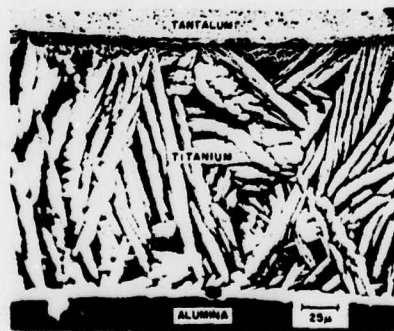


Figure 7 - Titanium Buffer Washer Seal of Tantalum-to-Alumina Prepared with Nickel Shims

interface and would undoubtedly leak due to the presence of many cracks. Such a structure is shown in Figure 8-A. If the same assembly is heated to a temperature of 1118°C , formation of the eutectic between TiNi and TiNi_3 will be observed. Upon cooling to room temperature, the seal will contain both of these phases in amounts dependent upon the temperature and duration of heating. A typical structure is shown in Figure 8-B. If, however, heating is continued to a temperature near, but not above, the highest eutectic in the system (the one between TiNi_3 and Ni), the formation of TiNi_3 at the interface will be promoted and TiNi will disappear. Heating to 1275°C for one minute will yield the structure shown in Figure 8-C, a seal which has been found to be very easily and reliably made and which possesses good mechanical strength and high-temperature capabilities. This seal contains a continuous layer of equiaxed TiNi_3 at the interface. If heating is carried a few degrees higher, the eutectic will form and degradation of the seal will ensue. Although heating for a few seconds above 1304°C will still yield leak-tight seals (Figure 8-D), longer heating times will cause a progressive decrease in the quality (vacuum tightness and mechanical strength) of seals produced.

It is thus clear that no general rules can be set forth with respect to the time-temperature relationship to be employed in active-alloy sealing, the effect of intermetallic phases on seal quality, or the high-temperature capabilities of a particular system of materials. The characteristics and limitations of each system must be experimentally determined with the help of equilibrium diagrams and metallographic examination of polished sections.

6. NEW TECHNIQUES AND APPLICATIONS

The need to more effectively utilize the high-temperature capabilities of ceramic-to-metal seals, as well as to develop improved sealing techniques, has recently been stimulated by the requirements of aerospace systems.

With the proper choice of materials and brazing alloys, the previously discussed sealing techniques are amenable to the fabrication of seals capable of sustained operation at temperatures to about 900°C . Most of the newer applications not only involve higher temperatures, but they expose the seal to corrosive vapors or liquids. Such is the case with seals for liquid-metal-cooled nuclear turboelectric generators, magnetohydrodynamic generators, cesium-vapor thermionic converters, and alkali-metal-vapor rectifier tubes.

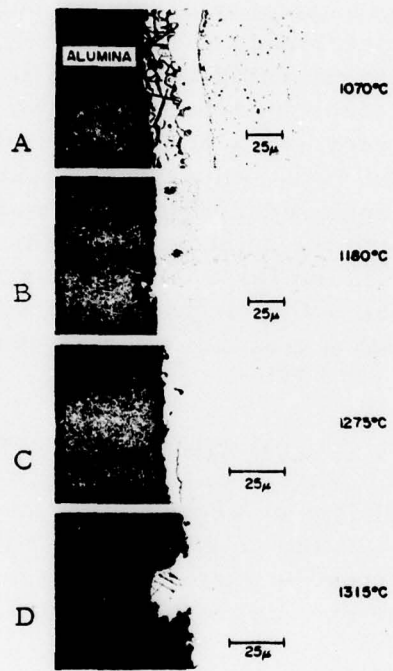


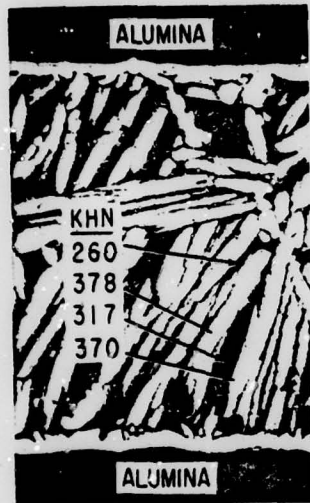
Figure 8 - Effect of Temperature on the Microstructure of Alumina-to-Nickel Seals Prepared with Titanium Shims

In the case of thermionic converters, the desired temperature of operation of the emitter-collector seal has risen steadily over the past several years from 600°C, a need which could readily be satisfied by several of the types of seals previously discussed, to the present requirement of 1500°C. Most of the structural metals and ceramics, as well as the sealing techniques used at lower temperatures, are totally unsatisfactory for use at temperatures in excess of 1000°C in the presence of alkali-metal vapors. For example, high-alumina ceramics, which are useful to temperatures well in excess of 1000°C in air, are rapidly attacked by alkali-metal vapors at this temperature. It is the silica-containing glass phase in such a ceramic which undergoes attack and the corrosion resistance improves as the silica content is decreased. For use at 1500°C, the silica content must be reduced to a few parts per million.

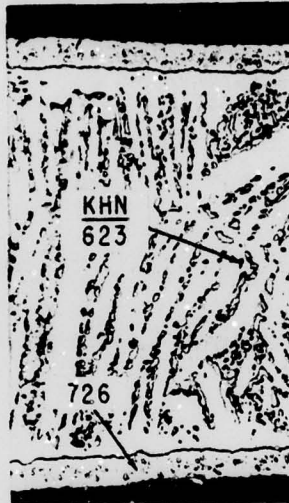
The molybdenum-manganese sealing techniques discussed in a previous section are, of course, useless since they rely upon the presence of silica in the ceramic or admixed with the coating to promote bonding reactions.

Although active-alloy seals can be readily made to silica-free ceramics, they suffer other limitations. For example, seals between titanium and pure sintered alumina are readily and reliably made by the nickel-shim active-alloy technique. Figure 9-A shows the microstructure of such a seal before test, and Figure 9-B shows the same seal after 1920 hours of exposure to a temperature of 700°C in vacuum. Continued reaction of the active metal titanium with the ceramic during testing has resulted in severe embrittlement by oxygen contamination. Although titanium shim seals of alumina-to-nickel, prepared so as to form $TiNi_3$ at the interface, are tolerant of somewhat higher temperatures, they are destroyed after long periods of time at 900°C due to solutioning of the $TiNi_3$ and loss of the strong $TiNi_3$ -alumina bond.

Many approaches to the development of high-temperature, alkali-metal-vapor resistant seals have been investigated, by a number of organizations, during the past several years. Many of these methods utilize some combination of heat and pressure, such as diffusion bonding, gas pressure bonding, electron beam welding or ultrasonic welding, to join both bare and metallized ceramic surfaces to refractory metals. Other investigators have utilized cermet powders or molten refractory oxides as "brazing" materials to join metals to ceramics.



A
BEFORE TESTING



B
1920 HRS AT 700 °C

Figure 9 - Titanium-to-Alumina Seals

One very useful technique has been the development^{26, 40, 41} of ultra-high-temperature, corrosion-resistant metallizing coatings for pure-alumina ceramics. The molybdenum and tungsten-based metallizing coatings developed by one group⁴² exhibit excellent adherence to pure alumina ceramics and vacuum-tight joints can be readily made thereto. The most useful coatings contain finely divided tungsten with admixed oxides which form a liquid phase of controlled composition and fluidity at the sintering temperature. Combinations of calcia, alumina and yttria have been found most useful as bonding oxides and, generally, constitute about two to ten weight percent of the coating. During sintering and upon cooling, growth of the alumina crystals at the interface occurs, firmly locking the coating to the substrate. In another approach²⁶ several percent of yttria is incorporated in the alumina ceramic and the coating is pure tungsten. The formation of yttrium tungstates is believed⁴³ to contribute to bond formation in this system.

Methods for joining these metallized surfaces to refractory-metal members, so as to fully utilize their high-temperature capabilities (coatings have been tested to 1500°C), are still under development.

The use of cermets in high-temperature seals has also received considerable attention.^{41, 42} A cermet may be defined as a heterogeneous combination of metals or alloys with one or more ceramic phases in which there is relatively little solubility at the preparation temperature.

By making a continuous or step-wise gradation in composition (volume fraction ratio of metal to nonmetal), it is possible to provide a shape having an electrically insulating core but with metallic surfaces to which metal members can be joined by braising or welding. This approach to sealing was first suggested by Knecht⁴⁴ and investigated under contract by a leading ceramic manufacturer.⁴⁵ Although they were primarily interested in low-cost methods for high-volume production of seals, and had considerable latitude in the selection of materials, many problems were encountered and the structures which were developed were never made available commercially.

Recently, insulating graded cermet structures with metallic surface layers have been successfully cold pressed and hydrogen sintered using blends of molybdenum and alumina powders.⁴² However, the large difference in thermal expansion between these two materials limits the rate of change of composition which can be used. The well-matched system niobium-alumina is not so limited but densification (sintering, hot-pressing, or gas pressure bonding) must be carried out in a good vacuum.

SEAL DESIGN

There are four basic types of seals whose identifying names are derived from the geometry of the seal and the component parts:

1. Concentric (also called cylindrical or outside) seals
2. Inside seals
3. Butt seals
4. Tapered seals.

In the following sections, we will examine the characteristics and limitations of each type of seal as well as the stresses which exist at several temperatures of interest.

In general, it is usually desirable that the metal and the ceramic be closely matched in thermal expansion in order to minimize the stresses which result from differential contraction of the two materials upon cooling from the brazing temperature. It is clear that as the residual stresses increase, the useful strength of a seal will decrease.

Let us briefly review some physical properties of metals which are of importance in seal design. When a force is applied to a metal it results in deformation or strain of the material. When this force is removed, the body returns to its original size and shape, provided that the unit stress developed by the force did not exceed the "elastic limit" of the metal. If the stress has gone beyond this limit, the body does not return entirely to its original dimensions but retains some permanent deformation or set. The yield point of steel, it will be recalled, is the load per unit area at which a marked increase in deformation (strain) occurs without increase in load. Many metals have no true yield point; consequently, a term called yield strength has been adopted as a measure of the onset of inelastic action. The yield strength is the stress required to produce a specified but arbitrarily selected amount of deformation (such as 0.2 percent-offset). The significant point about these terms is that they all relate to stresses which result in yielding or permanent deformation of a material.

Ceramics, on the other hand, are almost perfectly elastic solids and display nearly linear stress-strain curves up to the point of fracture. Thus, ceramic materials do not show elastic limits, yield points or yield strengths and it is the ultimate strength of ceramics which is of paramount importance. An important consideration is that the compressive strength of a ceramic is approximately ten times its tensile strength so that any stresses which are imposed should be compressive rather than tensile in nature. It is particularly important to minimize the stresses at the seal interface since this is usually the weakest link in the ceramic-metal seal.

The modulus of elasticity (E) is a very important consideration when selecting metals for seal making, and is defined as the ratio (within the limit of elasticity) of the stress to the corresponding strain:

$$E = \frac{\text{stress}}{\text{strain}} = \frac{\sigma}{e}$$

When a metal and a ceramic having different thermal expansions are rigidly sealed together at an elevated temperature and then cooled to room temperature, one or both of the materials must undergo deformation or strain if the seal is to remain intact. If it is assumed that all of the (elastic) deformation will occur in the metal, then the lower the modulus of elasticity of the metal used, the lower the unit stress which will effect this deformation.

If a metal with a low yield strength is used for sealing purposes, residual seal stress will be limited by plastic deformation when the stress which is generated by differential contraction exceeds the yield strength. Copper, for example, would deform plastically when the seal stress reached the 7000 psi yield strength of copper. Yield strength is not a fixed quantity, however, but decreases with increasing temperature. For example, the yield strength of commercially pure titanium decreases from a value of 60,000 psi at room temperature to 15,000 psi at 500°C. Type 430 stainless steel, by comparison, decreases from 40,000 psi to 30,000 psi over the same temperature range.

Thus, the coefficient of expansion and the modulus of elasticity determine the rate of buildup of stress, while the yield strength of the metal determines whether the deformation is elastic or plastic.

1. CONCENTRIC SEALS

This type of seal (Figure 10-A), also called the cylindrical or outside seal, is widely used in tube structures. Its proven reliability and ruggedness stems from the fact that in a properly designed seal, the ceramic-metal interface is under slight radial compression even at the elevated temperatures encountered during tube bakeout. The reason for this will be seen from an examination of Figure 11. This figure shows the thermal expansion of Type 430 stainless steel (17 percent chromium-iron alloy) and two low-loss ceramics used as tube envelope insulators. It is apparent that Type 430 stainless steel is a reasonably good expansion match for the forsterite ceramic so this system will be examined first.

Consider the events taking place in a typical 2-inch diameter concentric seal during brazing and subsequent cooling to room temperature. Assume a perfect fit of the metal sleeve to the ceramic cylinder at room temperature. During the heating portion of the brazing cycle, both ceramic and metal are undergoing thermal expansion, but at different rates. At the brazing temperature of 800°C , the metal sleeve will have expanded more than the ceramic and a gap of 0.001-inch will exist all around a 2-inch diameter insulator which must be filled by the brazing alloy. Upon cooling, no stresses will be set up until the freezing point of the brazing metal is reached. Below this temperature, the metal would like to contract at a greater rate than the ceramic but is restrained by the latter. This causes a "shrink fit" pressure or radial compression on the ceramic interface and a "hoop stress" or circumferential tension in the sealing sleeve. Assuming that the tensile hoop stress in the sleeve did not exceed the elastic limit at any time during cooling, it would be possible to reheat the seal to the melting point of the braze before all the radial compression on the seal interface is removed. Thus, during normal bakeout or during tube operation, the interface would never be placed in tension even though the metal sleeve might heat up somewhat more rapidly and, thus, expand at a slightly greater rate than the ceramic.

It was mentioned that no stress can begin to develop until the temperature has fallen to the freezing point of the brazing material, 778°C in the case of silver-copper eutectic alloy. If the sealing metal were clad with copper, as is often used to provide a surface having good electrical conductivity, solutioning of part or all of this cladding would be expected. Although this would not change the freezing point (solidus) of the resulting braze alloy, the liquidus temperature would be raised (from the 778°C eutectic temperature)

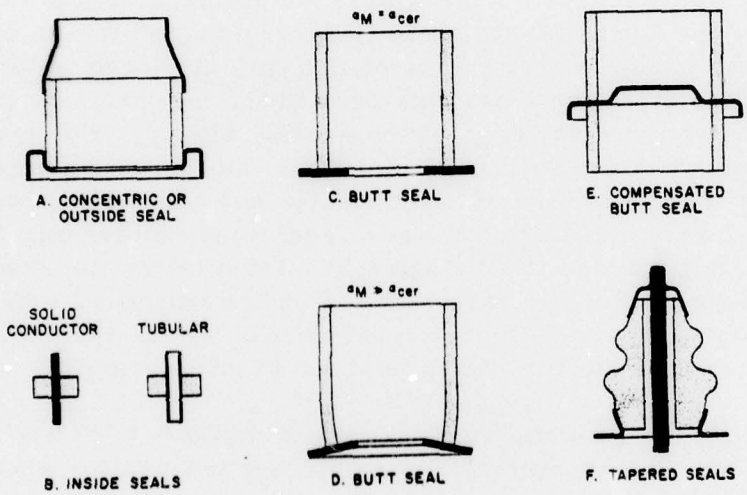


Figure 10 - Typical Ceramic-to-Metal Seal Designs

and freezing would occur over a temperature range. On the other hand, if brazing were being performed with an alloy of 35 percent gold-65 percent copper, solutioning of the copper cladding would raise both the liquidus and solidus temperatures. This can be readily understood by reference to the appropriate phase equilibrium diagrams.

If a high-alumina ceramic (94 to 99-percent alumina) were substituted for the forsterite in the seal of the preceding example, an entirely different situation would exist. At the brazing temperature, a gap of 0.0025-inch would exist all around the 2-inch diameter alumina insulator and must be filled by braze alloy. Upon cooling to room temperature, the difference in contraction of the Type 430 stainless-steel sleeve and the alumina would place the latter under severe radial compression. Were it not for the considerably higher strength of alumina ceramics, the insulator might be sheared off just beyond the edge of the sealing sleeve. For many applications, the higher dielectric constant of alumina ceramics would necessitate a reduction in the wall thickness of the insulator over that which would be permissible if a forsterite insulator were used, thus further aggravating an already serious condition. Although a reduction in the thickness of the sealing sleeve would reduce the radial stress on the ceramic, a better solution is to select a sealing metal more closely matching the thermal expansion of the alumina ceramic (Kovar, Ceramvar or 46 percent nickel-iron).

In the foregoing example, it was noted that a 0.0025-inch gap would exist between the 2-inch diameter ceramic and the sealing sleeve at brazing temperature. If this had been a 6-inch diameter seal, the gap would have been 0.0075-inch and it would have been necessary to reduce this clearance in order for capillary forces to hold the liquid braze metal in the joint. This can be accomplished by restraining the expansion of the sleeve by a band or wire wrapping of a lower expansion metal, generally molybdenum.

The preceding discussion of seals to Type 430 stainless steel has assumed that the elastic limit of the sealing metal was not exceeded or that plastic deformation of the brazing alloy did not occur during the cooling portion of the brazing cycle.

The mere fact that an expansion match exists between the metal and the ceramic at the solidus temperature of the braze does not assure a stress-free seal upon cooling to room temperature. In order to illustrate this point, let us examine several sealing systems in which a metal possessing a nonlinear thermal expansion behavior is used. Let us select, from a family of nickel-iron alloys, that composition which possesses the lowest total expansion to

the brazing temperature of 800°C. Although this alloy, 42 percent nickel-iron, is a fair expansion match to forsterite ceramics at 800°C, the two curves depart radically at low temperatures, as shown in Figure 12. It is this nonlinear expansion of the metal component which can be a source of trouble if concentrically sealed to a high expansion ceramic.

Upon examining Figure 12, it will be seen that the forsterite ceramic and the nickel-iron sleeve, if not sealed together, would contract equal amounts upon cooling to room temperature from the brazing temperature of 800°C. If, however, the ceramic and the sleeve are rigidly joined together at the brazing temperature, a different situation will exist upon cooling. During the first part of the cooling cycle, the metal would be contracting much more rapidly than the ceramic and the metal sleeve would be subjected to increasing circumferential tension. Under this stress, and particularly at elevated temperatures, yielding (plastic deformation) of the metal will occur. When the seal has cooled to the inflection temperature of about 400°C, the situation reverses itself and the rate of contraction of the ceramic becomes greater than that of the metal. If yielding had not occurred, this portion of the cycle would merely be relieving the circumferential tension which had been set up during the first part of the cycle and the seal would be stress-free upon reaching room temperature. Since, however, we have postulated yielding of the sleeve at some temperature above 400°C, the seal would reach the stress-free condition at a temperature somewhat above room temperature and cooling to room temperature would place the sleeve under circumferential compression and the interface under radial tension.

Since the nontransparency of ceramics precludes detection of seal stress by means of the polariscope, so valuable in glass-to-metal seal technology, other techniques have been sought with but moderate success. The ability of nonlinear metal expansion to cause radial tensile stress can, however, be crudely demonstrated by several means. One scheme utilizes the "split ring", originally developed to test the "fit" of a glaze to a ceramic; i. e., whether the glaze is stressed in compression or tension. In applying this ring test to seal studies, a metal sleeve is concentrically sealed to a ceramic ring of the same axial length. After scribing two reference marks on the ring, a saw cut is made through the sleeve and the ceramic ring between the two marks. The distance between the two marks before and after making the saw cut is a measure of the stress which exists in the sleeve; circumferential tension if the gap increases, compression if it decreases.

Let us now turn our attention to the use of alumina ceramics with several of these alloys which show nonlinear expansion behavior. The first

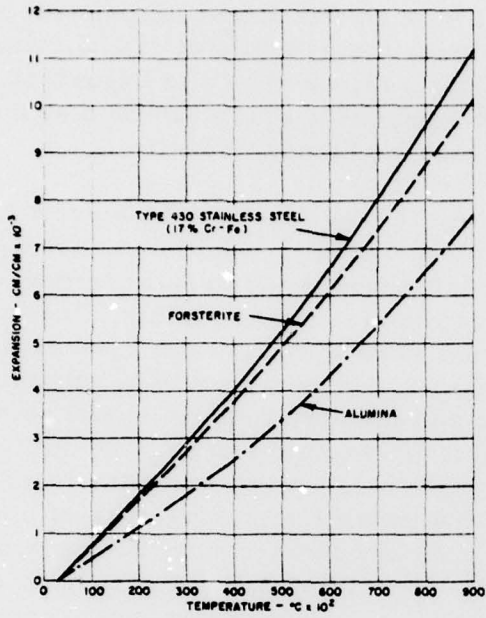


Figure 11 - Thermal Expansion of Alumina, Forsterite, and Type 430 Stainless Steel

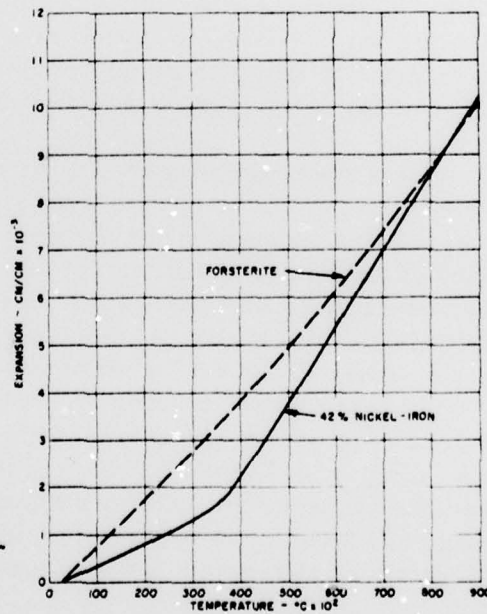


Figure 12 - Thermal Expansion of Forsterite and 42 Percent Nickel-Iron

to be examined is Kovar, a nickel-cobalt-iron alloy originally developed for sealing to hard glass but later adopted by many fabricators of ceramic-to-metal seals. Figure 13 shows that at the 800°C brazing temperature, the expansion of Kovar is but slightly higher than alumina, having crossed the alumina curve at about 600°C. Although it would at first appear that the greater total contraction of the metal would place a concentric seal under radial compression, tests and calculations have shown that such seals are either strain-free or in slight radial tension, due to yielding of the sealing sleeve during cooling.

Although it is generally considered desirable to maintain the interface of a concentric seal either stress-free or under slight radial compression, failure to do so should not cause undue concern. This is because the ultimate tensile strength of the bond is usually many times greater than the slight radial tension which would be developed in a mismatched seal such as discussed in the preceding paragraph. Bond strengths, measured in tension, can be expected to range from 1/2 to 3/4 of the tensile strength of the ceramic (20,000 psi to 30,000 psi for alumina) in a well made seal. Extensive acceptance of Kovar by the tube industry attests to its usefulness for sealing to alumina ceramics.

Kovar (Fervico) and Ceramvar, both Ni-Co-Fe alloys whose expansion curves are shown in Figure 13, have been found most useful for sealing to alumina ceramics. The 42-percent and 46-percent nickel-iron alloys shown in Figure 14, have also been widely used for concentric seals to alumina and are lower in cost. The 50-percent nickel-iron alloy would place a seal to alumina under severe radial compression and there would be danger of fracturing the ceramic if its wall were thin or the sealing sleeve were thick.

The choice of a metal to be used for ceramic-to-metal seals is dictated by a number of considerations in addition to that of thermal expansion. These include cost, thermal and electrical conductivity, strength, absence of phase transformations, workability and processing considerations. For sealing to forsterite, Type 430 stainless steel and 50-percent nickel-iron are useful, low-cost alloys which can be readily drawn or spun. Any chromium-containing alloy, such as the Type 430 stainless steel must, however, either be brazed in super-dry hydrogen or provided with a protective cladding. For sealing to alumina, 42-percent and 46-percent nickel-iron alloys are lowest in cost of the more desirable metals. In spite of the somewhat higher cost of the nickel-cobalt-iron alloys, they have been widely adopted because of their better expansion match.

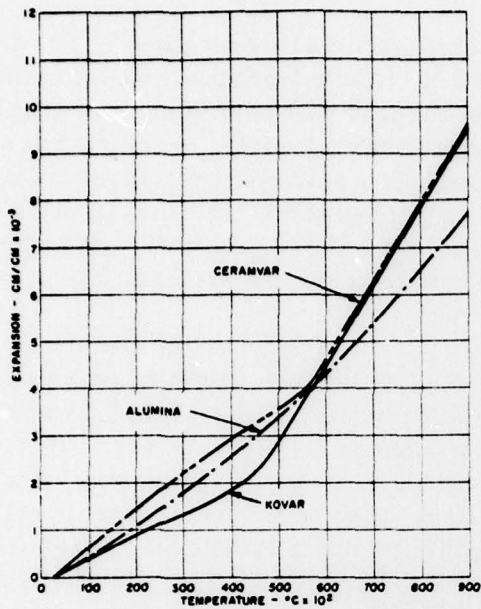


Figure 13 - Thermal Expansion of Alumina, Kovar, and Ceramvar

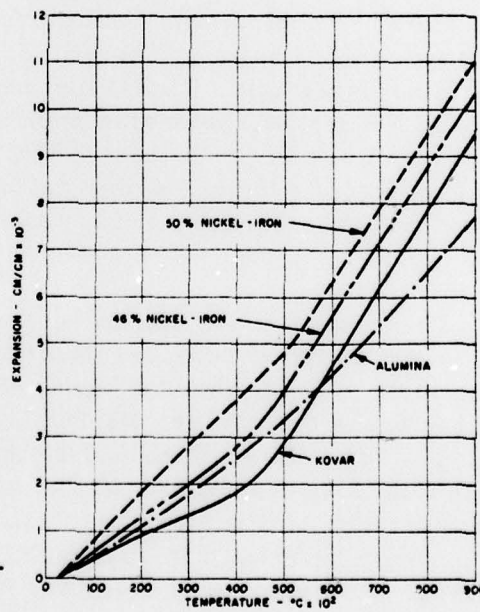


Figure 14 - Thermal Expansion of Alumina, Kovar, 46 Percent Nickel-Iron and 50 Percent Nickel-Iron

Niobium is an excellent thermal expansion match to alumina (Figure 15) and were it not for its high cost and the necessity for brazing in vacuum or inert atmosphere, it would be the best choice. Tantalum is a reasonably good match to alumina but, like niobium, cannot be brazed in the hydrogen atmospheres so widely used in the assembly of tubes and other electrical devices.

2. INSIDE SEALS

For lack of a better name, a seal in which a metal member is sealed through a hole in a ceramic is called an inside seal. The metal member, generally cylindrical in shape, may be hollow or solid but the seal design and materials used differ for each case (Figure 10-B).

As previously stated, ceramics are much stronger in compression than in tension. Thus, the design of any seal should generally be such that the ceramic, and particularly the metal-ceramic interface, is either not stressed at all or is stressed in compression. Exceptions to this rule are unavoidably encountered in inside seals.

Let us first consider the case of a solid conductor sealed within a hole in a ceramic insulator, probably the most troublesome of all ceramic-to-metal seals. Here it is desirable that the ceramic experience the same (or preferably a slightly greater) total contraction from the brazing temperature than the metal rod in order to place the latter, and thus the seal interface, under radial compression at room temperature. This, of course, stresses the ceramic insulator in circumferential and axial tension, the first exception to the general rule stated above. Such a seal will be successful, however, if the electrode is of small diameter; the expansion mismatch is not excessive; and the strength of the ceramic shape is adequate. Circumferential tension in the ceramic can be reduced by increasing the wall thickness but axial tension is not affected by changes in axial thickness.

There are few metals which adequately meet the requirements for inside solid conductor seals. Inside seals have been made between molybdenum and zircon ceramics as well as between molybdenum and alumina or forsterite ceramics. The former is a well matched system while the latter requires that the molybdenum rod be of small diameter (preferably not over about 0.040-inch diameter) or that a carefully controlled clearance between the rod and the hole be maintained in order to keep the circumferential tension in the ceramic to a safe value. The brazing alloy which fills this radial gap has a considerably higher expansion than the molybdenum rod and the radial expansion of the composite more nearly matches that of the ceramic. This is

similar to the use of Dumet wire for sealing through glass. Tantalum can be readily sealed through alumina, and titanium can be sealed through a matching forsterite, but brazing must be carried out in vacuum or an inert atmosphere.

In order to use low cost metals which do not match the expansion of the ceramic, it is necessary to select one with a low yield strength and to use it in the form of a thin walled tube. Thus, although the greater contraction of the metal (Figure 16) on cooling will subject the seal interface to tensile stresses, these stresses will be insufficient to rupture the bond and plastic deformation of the tube wall will occur. Nickel and copper are particularly useful because of their low yield strengths.

One novel approach to the problem of sealing a current-carrying member through a ceramic insulator consists of metallizing the entire outer surface of a ceramic rod, and brazing this rod into a metallized hole through a ceramic of the same composition as the rod. The thin layer of metallizing and solder thus provides a current-carrying path without upsetting the perfect expansion match between the rod and the insulator.

Still another, but similar, approach has been to prepare a metallic composite "alloy" which closely matches the thermal expansion of alumina. This is accomplished, for example, by liquid-phase sintering of a mixture of molybdenum and copper powders, proportioned in volume so that the aggregate thermal expansion matches that of the ceramic.

3. BUTT SEALS

In the case of butt seals, it is again possible to make a subdivision, based upon thermal expansion considerations, resulting in groups designated as matched and unmatched seals.

Figure 10-C shows a typical metal-ceramic butt seal. If the metal and ceramic members are well matched in thermal expansion there will be no differential contraction upon cooling from the solidification temperature of the braze alloy and the seal will be stress-free at room temperature. If the metal and ceramic parts do not possess identical thermal expansion characteristics, stresses will be introduced during cooling but may be partially relieved by plastic deformation (yielding) of the metal or brazing alloy, such as occurred in the cylindrical seals previously discussed.

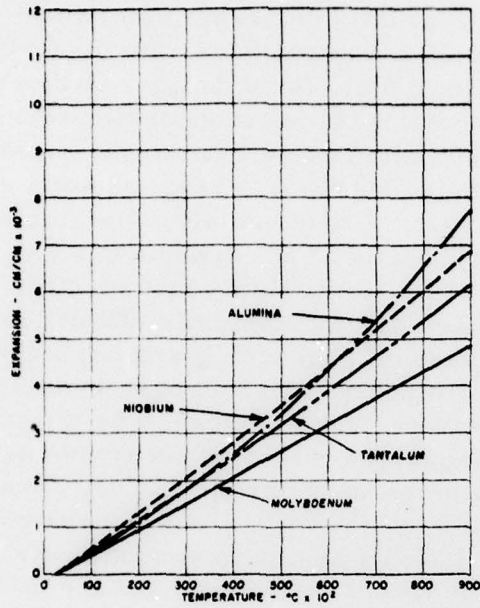
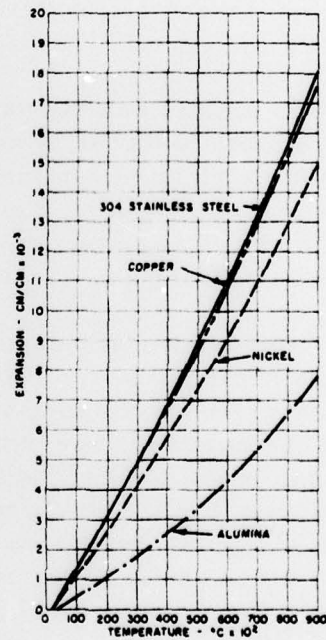


Figure 15 - Thermal Expansion of Alumina, Niobium, Tantalum, and Molybdenum

Figure 16 - Thermal Expansion of Alumina, Nickel, Copper and Type 304 Stainless Steel



Although expansion matching is usually desirable, those few metals for which matching ceramics are available possess certain disadvantages which often limit their use. Titanium metal, for example, is closely matched in thermal expansion by specially formulated forsterite ceramics and this system of materials has been extensively used in the construction of voltage-tunable magnetrons, voltage-regulator tubes, ceramic receiving tubes, and other electronic components. Unfortunately, titanium has an electrical conductivity less than 4 percent that of copper and an equally poor thermal conductivity. In addition, seals to titanium must be made in vacuum or an extremely pure inert atmosphere due to titanium's affinity for oxygen, nitrogen, and hydrogen. Although vacuum processing and sealing offers certain advantages over the more commonly used hydrogen brazing approach to seal assembly, it has not yet met with wide acceptance by the industry. Molybdenum, which possesses an expansion match in the zircon ceramics is costly, difficult to shape, and oxidizes in air above 500°C. Tantalum and niobium, which are good matches for the high-alumina ceramics, are also expensive and, like titanium, must be sealed in vacuum. As the demand for niobium in the aerospace industry increases, and the cost decreases (as occurred for titanium) it will, undoubtedly, find increasing use in the manufacture of seals. This will occur because alumina is an excellent, low cost, high strength, insulating material and no other metal offers the needed properties of excellent expansion match, high strength and good workability.

The metals and alloys which are currently most used for sealing, because of their low cost, good electrical conductivity, and ease of working, do not have matching ceramics and seals made from them are, therefore, termed unmatched seals. Such metals as copper, nickel, Kovar, Ceramvar, nickel-iron alloys and chrome-iron alloys are mated with ceramics such as steatite, forsterite, zircon and alumina in unmatched butt seals.

Consider the stresses which arise from sealing a disk or ring of metal to a mismatching ceramic cylinder (Figure 10-D, greatly exaggerated). If the contraction of the metal from the brazing temperature is greater than that of the ceramic, shearing stresses will be generated at the ceramic-metal interface and the bending moment will cause an axial tensile stress to be introduced in the surface of the ceramic a short distance from the interface. If the mismatch is great, residual stresses may be limited by plastic deformation of the metal, and the magnitude of the residual stress will be related to the yield strength of the metal and its temperature dependence.

If another ceramic cylinder of the same diameter and wall thickness is sealed to the other side of the metal washer of the preceding example,

the seal is said to be "symmetrical", "compensated", or "backed-up" (Figure 10-E). In this case, the residual stresses are now shared by two ceramic cylinders. This method of reducing the unit shearing stress and the minimizing of bending moments was first demonstrated by Housekeeper³ while working with seals of copper to glass.

Compensated as well as uncompensated butt seals are stressed in shear if the component parts are unmatched in expansion (the usual case) and it is necessary to design the metal member in such a manner that the residual stresses are lower than those which will fracture the joint. Low unit shearing stress in the seal is obtained by using a metal of low modulus of elasticity and/or low yield strength, as close an expansion match as is possible, and a minimum amount of metal which must undergo strain.

The latter requirement is met by using thin metal members with a minimum volume of material in the plane of the seal; for example, by using a flanged cup instead of a solid disk. Although a metal washer having the same inside and outside diameters as the ceramic would be the most favorable situation, such a configuration is rarely useful. In most cases, the metal member extends inward to support internal portions of the device and may extend outward beyond the surface of the ceramic to permit attachment to other members or to facilitate electrical connection. These inwardly and outwardly extending portions apply additional stress to the volume of metal sandwiched between the two ceramics. In such cases, increasing the wall thickness of the ceramic will reduce the unit shearing stress at the interface. If the metal member were a simple washer having the same diameters as the ceramic, the unit shearing stress would be essentially independent of the wall thickness of the ceramic.

The maximum strength which can be achieved in a ceramic-to-metal seal is equal to the strength of the ceramic. This ultimate value of strength is reduced by any stresses which are introduced by thermal expansion mismatch. From the relationship $\sigma = Ee$, it can be seen that a low modulus of elasticity results in a low residual stress for any given amount of strain (proportional to the thermal expansion mismatch).

Residual stress can also be kept to a low value, in spite of a large difference in expansion between the metal and the ceramic, by selecting a metal with a low yield strength, thus limiting the stress by plastic deformation. Copper, nickel, gold and silver admirably meet this requirement, particularly since they would be fully annealed upon reaching the brazing temperature. It is the very low yield strength of gold (high expansion) which permits its being sealed to fused silica, a brittle glass with an extremely low coefficient of thermal expansion.

In cases where the design or thickness of the metal member would impart severe shearing stresses to the ceramic, use can be made of ductile copper "buffer" washers on each side of the metal to limit the stress through plastic deformation.

4. TAPERED SEALS

Tapered seals, as in Figure 10-F, may be looked upon as modifications of the concentric seal. Although the use of conically shaped parts minimizes the necessity for close diametral tolerances on the ceramic and metal parts, it introduces other problems. The taper angle must be held within close limits, the parts are no longer self-jigging (particularly at large taper angles) and control of the over-all length of the seal is more difficult. Furthermore, the application of uniform metallizing coatings, particularly by mechanical means, is virtually impossible.

Thin-walled ceramic cylinders generally undergo some warpage during the maturation firing, and centerless grinding of the fired insulator is employed in order to provide a dimensionally correct, truly cylindrical surface for the making of a concentric seal. In the case of tapered seals, where plunge grinding of the taper would be quite expensive, it is desirable to eliminate grinding by making the wall thickness great enough to minimize warpage. Such is the design of the insulators generally used in the taper seals of transformers and capacitors, two large volume applications for such seals.

BIBLIOGRAPHY

1. "Glass-to-Metal Seals", J. H. Partridge, the Society of Glass Technology, 1949
2. "Materials and Techniques for Electron Tubes", Walter H. Kohl, Reinhold Publishing Corp., 1960
3. "The Art of Sealing Base Metals Through Glass", W. G. Housekeeper, J. Amer. Inst. Elec. Engrs., 42, 954-960, 1923
4. "Glass-to-Metal Seals in Electronic Components and Applications", A. J. Monack, Electrical Manufacturing, February 1947
5. "Glass-to-Metal Seals", A. W. Hull and E. E. Burger, Physics, 5 (12) 384-405, 1934
6. "Glass-to-Metal Seals II", A. W. Hull, E. E. Burger, and L. Navias, J. Appl. Phys., 12, 698-707, 1941
7. "The Effect of Temperature Treatment on Glass-to-Metal Seals", J. T. Littleton, Jour. Amer. Ceram. Soc., 18 (8), 239-245, 1935
8. "Metallizing Glass and Ceramic Materials", A. J. Monack, Glass Industry, 28 (1) 21, 1947
9. "High Temperature Match-Box Electron Tubes", Westinghouse Electric Corp., Contracts DA 36-039 SC-87404 and DA 36-039 SC-75076, 1961-1962
10. "Electron Tube", L. P. Garner, U.S. Patent 2,909,698
11. "Development of the Radial Compression Seal", L. E. Martin and A. C. Tunis, RCA Engineer, 3 (3) 9-11, 1957-1958
12. "A Critical Survey of Methods of Making Metal-to-Ceramic Seals", R. Wellinger, Univ. of Illinois, Electron Tube Research Lab., April 30, 1949

13. "Ceramic Receiving Tube Refinement Program", Eitel-McCullough, Inc., Contract AF 33(600)-36699, ASD TR 61-268, November 1961
14. H. Vatter, French Patent 817,308, September 1937; U.S. Patent 2,139,431, December 1938
15. H. Vatter and H. Hinderer, Canadian Patent 399,489, 1941
16. "Ceramic-to-Metal Seals", Hans Pulfrich, U.S. Patent 2,163,407 and 2,163,410
17. Telefunken Metal-Ceramic Radio Tubes, G. L. Hunt, B.I.O.S. Final Report 30, PB-18, 901, 34 pp, August 1945
18. New Vacuum Tube Techniques of the Telefunken Rohrenwerke, Berlin, M. J. Gross, F.I.A.T. Final Report No. 560, PB-17, 553, December 1945
19. "Metallizing and Ceramic Sealing with Manganese", Television Eng., H. J. Nolte and R. F. Spurck, 1, (11), 14-18, 1950
20. H. J. Nolte, U.S. Patents 2,667,432 and 2,667,427
21. "Metallized Ceramic Member and Composition and Methode for Manufacturing Same", R. H. Bristow, U.S. Patent 3,023,942
22. (a) "Metal-to-Ceramic Seal Technology Study", Final Technical Report, S.S. Cole et al, Sperry Gyroscope Co., Contract AF30-(602)-2047, June 1959 to September 1960
(b) "Ceramic-to-Metal Seals for High-Power Tubes", Final Technical Report, C. Johnson et al, Sperry Gyroscope Co., Contract AF 30(602)-2371, April 1961 through October 1962
23. "The Mechanism of Ceramic-to-Metal Adherence", A. G. Pincus, Ceramic Age, 63 (3) 16-22, 30-32, 1954
24. "Metallographic Examination of Ceramic-Metal Seals", A. G. Pincus, Journal Amer. Ceramic Soc., 36 (5) 152-158, 1953
25. "An Investigation of Bonding Mechanisms of Ceramic-Metal Seals by Electron Microprobe Techniques", H. Schreiber, Jr., and W. C. Lo. Presented at the 65th Annual Meeting of the American Ceramic Society, 1963

26. "Ceramic Materials for Nuclear Thermionic Converters", R. E. Cowan and S. D. Stoddard. Presented at the 65th Annual Meeting of the American Ceramic Society, 1963
27. "Metallurgical Research and Development for Ceramic Electron Devices", Contract No. DA 36-039 SC-90903, Eitel-McCullough, Inc., 1962-1963
28. "High-Temperature Metal-Ceramic Seals", H. Bender, Ceramic Age, 63 (4) 15-24, 1954
29. "Fabrication of Metal-to-Ceramic Seals", A. J. Chick, et al, U.S. Patent 2,708,787
30. "Effect of Composition and Crystal Size of Some Alumina Ceramics on Metal-to-Ceramic Bond Strength", J. R. Floyd. Presented at the 64th National American Ceramic Society Meeting, 1962
31. "Some Parameters Affecting Ceramic-to-Metal Seal Strength of a High-Alumina Body", S. S. Cole and J. J. Hynes, Bulletin Amer. Ceramic Soc., 37 (3) 135-138, 1958
32. "Metal-Ceramic Interactions: III, Surface Tension and Wettability of Metal-Ceramic Systems", M. Humenik and W. Kingery, J. Amer. Ceramic Society, January 1954
33. "Interface Reactions Between Metals and Ceramics; I. Sapphire-Nickel Alloys", W. M. Armstrong et al, Jour. Amer. Ceramic Soc., 45 (3) 115-118, 1962
34. "Metallizing and Bonding Non-metallic Bodies", Floyd C. Kelley, U.S. Patent 2,570,248, 1951
35. "Metal-Ceramic Brazed Seals", R. J. Bondley, Electronics, 20 (7) 97-99, 1947
36. "Metal to Nonmetallic Brazing", C. S. Pearsall and P. K. Zingesser, M.I.T. Research Lab. of Electronics, Technical Report No. 104, April 5, 1949
37. Handy and Harmon, Bridgeport, Conn.; U.S. Patent 2,739,375, C. D. Coxe, "Joining of Non-metallic Materials and Brazing Filler Rods Therefor"

38. "Sealing Metal and Ceramic Parts by Formation of Reactive Alloys", J. E. Beggs, Transactions IRE, CP-4, March 1957, 28-31
39. "Vapor-Filled Thermionic-Converter Materials and Joining Problems and Plasma Research Pertinent to Thermionic-Converter Operation", R. H. Bristow, M. J. Slivka, M. O. Gibbons, Final Technical Summary Report, Contract NObs-86220, December 1962
40. "Research and Development Program of Thermionic Conversion of Heat to Electricity", R. H. Bristow, Final Technical Summary Report, Vol. I, General Electric Co., SPNSO Report GEST-2035, Contract NObs-88578, June 1964
41. "Ceramic-to-Metal Seals for High-Temperature Thermionic Converters", M. L. Dring, The Bendix Corp., Contract AF33(657)-10038, RTD-TDR-63-4109, October 1962 through September 1963
42. "Research and Development Program of Thermionic Conversion of Heat to Electricity", R. H. Bristow, R. D. Hanna and K. P. Zeman, Technical Summary Report, General Electric Co., SPNSO Report GEST-2046, Contract NObs-90496, December 1964
43. "Mechanism of Adherence of Tungsten to Bodies Containing Yttria", R. E. Cowan, C. C. Herrick and S. D. Stoddard. Paper presented before the Amer. Ceramic Society, September 17, 1964
44. "Application of Pressed Powder Techniques for Production of Metal-to-Ceramic Seals", W. L. Knecht, Ceramic Age, 63 (12-13), 1954
45. "Ceramic-to-Metal Seals by Pressed Powder Techniques", H. C. Dunegan, American Lava Corp., Final Report on Contract AF33(600)-27329, December 1956