Proceedings of the

THIRD NATIONAL CONFERENCE ON

TUBE TECHNIQUES

September 12, 13, 14, 1956
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"Survey of Ultra-High Vacuum Techniques," by L. J Varnerin, Westinghouse Electric Corporation

Contents

SESSION I R. J. Bondley, *chairman*

SESSION II A. M. Andrus, *chairman*

SESSION III J. A. Becker, *chairman*

SESSION III continued

SESSION IV W. G. Shepherd, *chairman*

SESSION V L. L. Kaplan, *chairman*

SESSION VI T. E. Hanley, *chairman*

Proceedings of the

Third National Conference on Tube Techniques

1. A Survey of the Application of Ceramics as Vacuum-Tube Envelopes

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The use of ceramic shapes as vacuum-tube envelopes has pyramided rapidly in this country during the last ten years in the development and production of a wide variety of tube types, such as receiving, gaseous discharge, power, and microwave devices. Some of these developments have taken advantage of the adaptability of ceramics to mechanized assembly and/or to rugged construction; others, of the desirable high-temperature bake-out properties of ceramics. Obviously, despite the current designs or approaches, the many advantages of these refractory bodies are well recognized and it can be safely assumed that the replacement of glass by ceramic will continue to increase.

While a few serious attempts to apply ceramics to vacuum-tube construction were initiated during the late thirties, it was not until after the war period that practical processes were developed. The "moly" or "Telefunken" process was first reported by British survey teams investigating the German technology at the conclusion of the war. The titanium process, sometimes referred to as the "Bondley" process, was developed and was first reported in the literature in 1947. These two processes have been further developed and refined, but the fact remains, that they are used in practically all the experimental and commercial production of metal-ceramic seals at the present time. Figure 1 illustrates a cross-section of a moly seal.

The moly process depends on the diffusion and reaction processes of finely divided molybdenum powder, either metallic or oxide, as the bonding medium. These powders are applied to the ceramic surfaces by any convenient means, such as spraying, painting, silk-screen printing, etc., and are then hydrogen-fired to develop the bond. Almost any organic vehicle may be used for suspension of the powders that is suitable for the particular method of application. The essential requirements of such a vehicle are (a) viscosity high enough to prevent settling of the suspension, (b) a low residue of carbon resulting from the firing schedule, and (c) a proper drying range satisfactory for the method of application. The firing process is accomplished in the range of temperatures from 1100 to 1300°C; and the water content of the hydrogen is carefully controlled by assuring the saturation of the hydrogen at some temperature above ambient, generally in the range of 40 to 60°C. The elapsed time of the firing process must be sufficient to permit the diffusion of the molybdenum metal and/or oxide into the surface of the ceramic to complete the bond but insufficient to cause partial oxidation of the molybdenum metal surface. As mentioned previously, the oxide (Mo_2O_5) or salts (such as ammonium molybdate) have been used quite successfully. They do require a much drier hydrogen atmosphere. However, most of the experimental and commercial applications of this method use finely divided metallic powder in which the particle size, in the range of 3 to 10 microns, is carefully controlled. The thickness of the coated film of powder on the ceramic surface must be sufficient to furnish ample material for the diffusion processes and insufficient to leave excess material which will be improperly bonded and/or sintered to the surface. The usual range of thickness approximates 1 mil.

The resultant molybdenum surface, as indicated in Fig. 1, should have a smooth metallic luster, be reasonably abrasion resistant, and, of course, well bonded. This surface is then generally coated with nickel either by electroplating or by applying nickel powder and subsequently firing at 800 to 1000°C in dry hydrogen. The purpose of this nickel surface is to provide a clean metal surface that is readily wet by the brazing alloy and to retard the complete alloying of the moly which would destroy the bond. The usual brazing metals are copper, or the copper-silver eutectic (i.e., BT), although various other alloys of silver, gold, copper, and nickel are used. The requirements of a good brazing alloy are its ability to readily alloy with the metallic surface, to have a low diffusion rate into that surface with a high fluidity at the temperature of brazing.

While this moly process may be used with almost all the ceramic bodies, the general trend has been to use it with alumina-base ceramics. These alumina

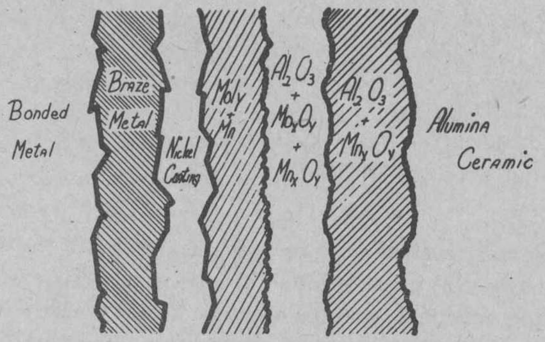


Fig. 1. Cross section of a molybdenum-manganese bond.

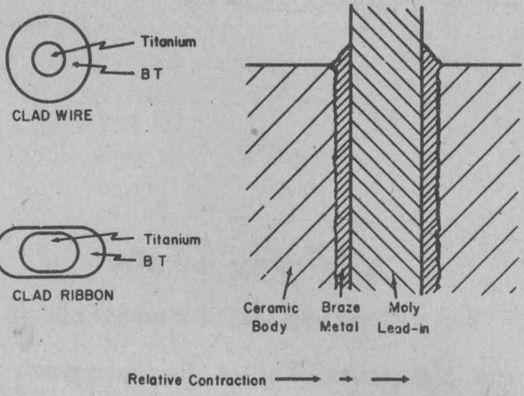


Fig. 2. Titanium sealing with BT-clad wire.

bodies range from 85 to 98 per cent alumina content, the 95 per cent body being the most generally used. Its advantages are the ability to withstand high temperature, high strength at temperatures and low coefficient of thermal expansion. Its main disadvantage, because of its high hardness on the Moh scale, is that it is difficult and costly to cut or grind the surface, as the use of diamond powder as the abrasive medium is required.

The bonding of the molybdenum coating to alumina bodies is enhanced by the use of 5 to 10 per cent of manganese metal powder mixed with the molybdenum powder. The manganese, because it has a higher difussion rate into the alumina body, yields stronger and more consistent bonds. It has been shown upon microscopic examination of these molymanganese coatings on alumina that the manganese has penetrated into the alumina to a depth of about 5 mils, and has noticeably changed the crystal structure of the ceramic.

The titanium process, as originally developed, depended on the active, nascent surface produced by the decomposition of titanium hydride as the bonding medium. This surface is readily wet by most metals and alloys, providing the activity of the surface is not destroyed by oxidation before the brazing metal has melted and wet the surface. Thus, it is very difficult to make brazes with copper and nickel because the titanium is at least partially oxidized before the temperature of the system can be raised to the melting point of the brazing metal. It is for this reason essential to have a good vacuum (better than 10^{-4}) or an extremely dry noble gas atmosphere and, further, to have a brazing metal with a melting point below or only slightly higher than the decomposition temperature of the hydride, about 650°C.

The recent development of BT-clad titanium wire permits the making of seals without precoating the ceramics and under less stringent conditions as concerns available oxygen in the surrounding atmosphere. Such a seal is shown in Fig. 2. This cladding is accomplished by drawing a tube of the brazing metal (e.g., BT) over a rod of titanium metal and reducing the combination to the desired wire size. Relief of the coldwork is readily accomplished by ordinary annealing in dry hydrogen or rare gas atmospheres, as the titanium is amply protected from the atmosphere by the cladding metal. The clad wire is normally in the range of size of 2 to 5 mils and of analysis of 5 to 10 per cent by weight of titanium. Due to the difference in densities of the two metals, this results in a wire in which the titanium is about 30 per cent of the diameter. This latter fact effectively precludes the use of flattened or rolled wire, as the cladding would be deformed preferentially to the titanium core, exposing it to the ambient atmospheric conditions prevailing during the brazing operation. However, where ring-shaped wire preforms are adaptable to a given process, they are quite successful and have several applications.

The use of alloys of titanium has been restricted by the lack of malleability of alloys containing more

HEATS OF FORMATION
$\Delta Hf°$ – KILOCAL

IVa	Va	VIa	VIIa
SiO_2 205			
TiO_2 218	V_2O_5 373	Cr_2O_3 269 CrO_3 138	MnO_2 124
ZrO_2 258	Nb_2O_5 463	MoO_3 180	
CeO_2 233	––––––– Rare Earths	–––––––––––	
HfO_2 271	Ta_2O_5 500	WO_3 201	
ThO_2 292		UO_3 302	

than 5 per cent of titanium, which appears to be the minimum titanium content capable of promoting the bond. Furthermore. the pulverizing and powdering of the brittle higher titanium alloys has not been completely developed because of the difficulty of retarding the superficial oxidation of the powder, which decreases its bonding activity. The eutectic alloys of titanium with copper, nickel, and managanese have melting points under 1000°C, are hard, and easily pulverized; and in the massive state, they do have excellent flow and wetting properties on the ceramic bodies. It would seem that further development in this field is warranted and could be very fruitful.

Another method of producing titanium seals is by the use of shims of titanium between the ceramic and a metal forming a low-melting eutectic with the titanium. At the temperature of sealing, the eutectic is formed, permitting rapid migration of the titanium into both the ceramic and the metal; this latter step again raises the melting point of the eutectic as the titanium content decreases. The resultant seal is effectively limited during processing and operation only by the temperature of the melting point of the base metal.

One other seal that has been used commercially is the so-called "pressure seal." This consists of pressing a high-strength ceramic cylinder into an alloy steel cylinder having high strength at the highest temperature of use. The junction sections of the two cylinders are accurately finish-ground to a slight taper, so that the resultant seal might be likened to a Johansen block seal under continuous high pressure.

It is rather startling, at least from the research point of view, that only the two elements, titanium and molybdenum, are capable of promoting a bond. As shown in the periodic table, their positions are widely separated and truly indicate their dissimilar properties. One may rightly question why the use of zirconium has been unsatisfactory in this application; it certainly has not been due to lack of developmental effort. By the same token, vanadium, chromium, and perhaps tungsten should be effective as bonding mediums. Undoubtedly, the answer lies not only in their relative periodic position or their heat of formation of the oxide, but also in their other physical properties, such as their rate of diffusion in the ceramic oxides. At least experimental effort in these directions is being carried on in several laboratories, such as the ceramic sections of the Massachusetts Institute of Technology and the National Bureau of Standards. Both of these laboratories are using the experimental approach of determining the wetting angle of the alloys on single ceramic oxides in an effort to determine the mechanism and obtain a better understanding of the bond.

The mechanical properties of these bonds should, in all cases, equal those of the ceramic, which should always be the weakest member of the system. The main requirement for obtaining this condition is that the coefficients of thermal expansion of the materials should be reasonably matched so that the bond or seal is always subject to a compression force which does not exceed the strength of the ceramic. As the seal is always produced at the brazing temperature, the forces of contraction from that temperature must be properly engineered. Such engineering approaches are (a) the proper thickening of the ceramic or thinning of the high-expansion metal when the latter is external to the ceramic, as by the use of cylindrical or planar diaphragms; (b) the use of highly ductile soft metals, which in contracting cannot exceed the strength of the ceramic; (c) the proper proportioning of the combined coefficients of the braze and sealed metals to that of the ceramic, especially in the lead-in pin seals through the ceramic; (d) retention of thin seals in ceramic-to-ceramic combinations so that the metal does not have too much volume and therefore excessive strength; or (e) the development of a ceramic with a coefficient matching a given metal combination. It should be further emphasized that the temperature-related strength of these seals should be only affected by the thermal conductivity of the ceramic body which limits the temperature rate-of-change, and not by the range of temperatures. This latter range is the main advantage of the metal-ceramic seal in that it includes the effective range from the brazing temperature to that of alcohol-dry ice. In this connection, it should be mentioned that the use of an external metallic anode in a metal-ceramic device severely limits the temperature-operational advantages of the device due to temperature corrosion of the metal portion of the envelope. Of course, this observation does not apply to those instances where the immediate associated circuitry cannot withstand higher temperature operation, such as in microwave devices.

The "cook-book" art of the production of metal-ceramic seals is the usual but unfortunate commentary on such developments. While several industrial laboratories have investigated these bonds, little if any factual information on the actual mechanism has resulted and been reported in the literature. Most of this effort has merely enhanced the practical application of the art. For the further improvement of the art, fundamental investigations are needed of diffusion rates of both metals and oxides in metallic and oxide mediums and of phase diagrams of ternary alloy systems and vapor pressures of these alloy systems. Applied research must then use this information and develop the limiting boundaries for the bonding mechanisms. Then and then only, will the engineer have a comprehensive understanding of the methods and limitations of his successfully applied process.

The main advantages of metal-ceramic seals are (a) ruggedness and strength, (b) high-temperature strength, (c) permissable high-temperature bake-out during evacuation, (d) no stress anneal required, and (e) dimensional stability. Unlike the glasses, ceramics have strength and rigidity throughout a wide temperature range, from below room temperature to more than 1000°C; and furthermore due to their structure, they are not subject to temperature-induced stresses and therefore require no annealing. While ceramics do have a negative temperature coefficient of strength, it is smaller than that of either the metals or the glasses.

Perhaps the greatest advantage in the use of ceramics is the fact that the evacuation and also sealing process may be accomplished at temperatures up to 1000°C. It will be recalled that the glasses are still releasing enormous quantities of gas (mostly water vapor) at the maximum temperature of bake-out (350 to 400°C). On the other hand, it is believed that at temperatures of 800 to 1000°C, the ceramics have passed their peak of gas evolution and are quite thoroughly degassed. This is indicated, if not proved, by the general concensus that getters are not required to maintain excellent life characteristics even at elevated temperatures (300 to 500°C). It is generally believed that there are two facets to this advantage, namely, the thorough degassing at the sealing temperature and, because of this degassing, all the interior surfaces are equally ravenous for the gases evolved during life. Thus these evolved gases are tenaciously absorbed by these clean surfaces, and this process is sufficient to maintain the vacuum at the desired degree.

Dimensional stability is another valuable contribution of ceramic construction. In other words, once the ceramic part is formed or ground to shape and size, the engineer is assured that no changes will occur during processing and that the ceramic will retain its dimensions even better than a piece of metal. Thus, the engineer can predict maintenance of spacing of the electronically active parts during assembly and processing.

In those cases where a reasonable match between metal and ceramic expansions is undesirable or impossible, the use of a soft metal will permit a satisfactory bond. Thus, metallic lead, with titanium hydride, will bond copper to alumina, steel to pyrex, and sapphire to pyrex. In the extreme cases of mismatch, it is neces-

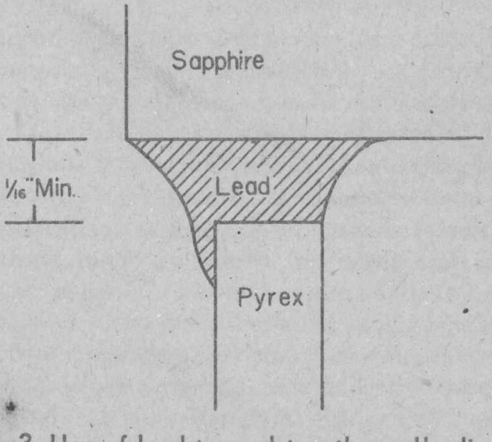


Fig. 3. Use of lead to seal two thermally dissimilar substances: pyrex and sapphire. See also Fig. 4.

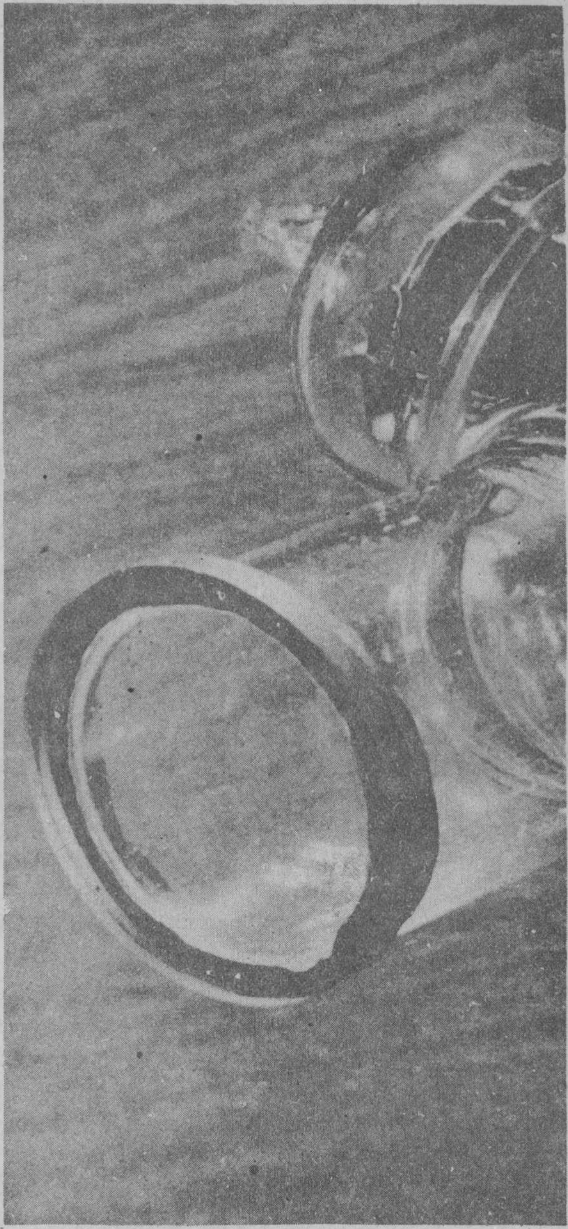


Fig. 4. Use of lead to seal two thermally dissimilar substances: pyrex and sapphire. See also Fig. 3.

sary to have a definite thickness of lead to take up the stresses as shown diagrammatically in Fig. 3 and pictorially in Fig. 4. This technique has also been used for sealing periclase (MgO) windows: and it is indeed unfortunate that we lack a higher-melting metal with physical properties similar to those of lead.

The main disadvantage in the application of ceramics is in their fabrication to controlled dimensions because of their variable shrinkage during the firing process. Due to this shrinkage, the design of ceramic pieces must be such as to permit the widest tolerances possible and to require close tolerances only in those dimensions that can be finished by grinding. Of course, grinding of alumina is expensive and, for this reason, it is desirable to weigh the more economical grinding of the Forsterite bodies against their lower strength. The other disadvantage, the matching of expansion coefficients, is not new to tube engineers, and in this case, it is only necessary to remember that ceramics have limited strength and effectively no ductility.

The following examples of developmental and commercial application of metal-ceramic seals depict a few instances of the progress to date. One of the first applications of ceramics was to replace glass in the 2C39. This development was carried on simultaneously by several companies under military sponsorship and has resulted in the availability of a tube with increased operational characteristics. Figure 5 shows the development of the CD-8 by the Eitel McCullough Co., which is notable for its planar, multiceramic ring structure. This program has resulted in the development of several tube types suited for mechanized production. Figure 6 shows the development of the General Electric Co., which was publicly released during the past year. It is notable for its small size, high efficiency, high-frequency operation, and for the development of a matching ceramic-metal seal. Figure 7 illustrates the application of ceramic to klystrom production by Varian Associates, who claim increased uniformity of operational life. Figure 8 shows the Type 2332A of the Radio Corporation of America illustrating the use of the pressure seal, previously mentioned. The combined requirements of high-power and stable-discharge characteristics have been met in the development of a metal-ceramic hydrogen thyratron by Edgerton Germeshausen and Grier, Inc., as shown in Fig. 9.

These examples are not meant to include all the applications nor to indicate all the companies active in this field, but merely to survey a few of the outstanding applications in the field of electronic devices.

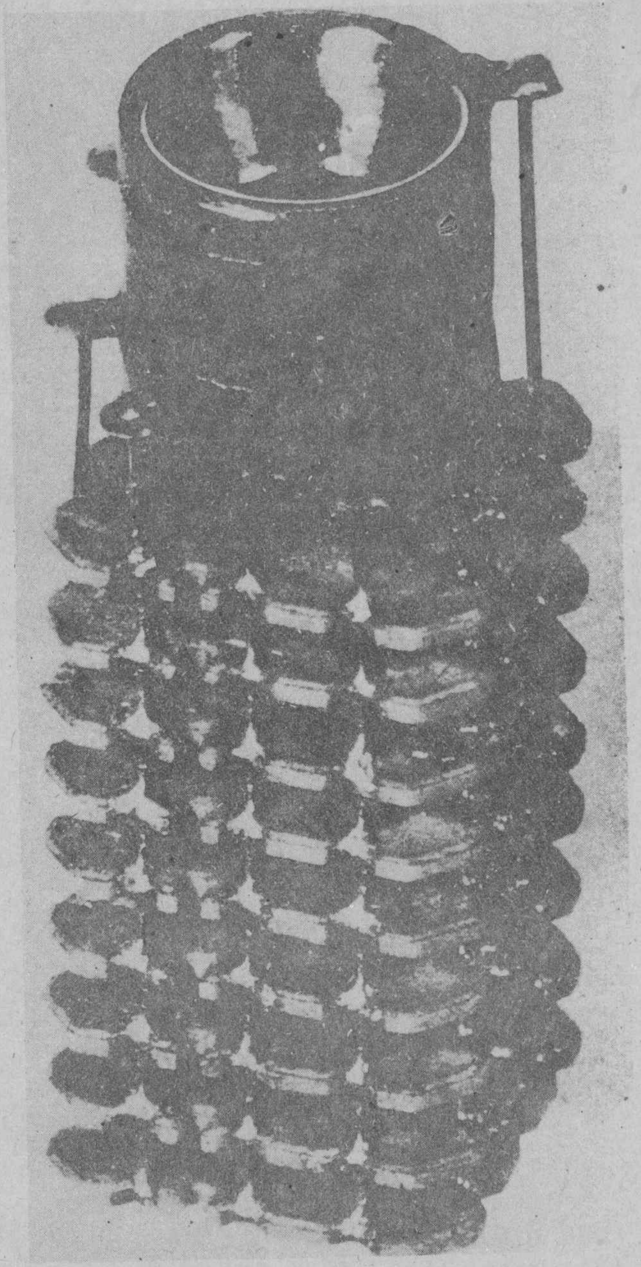


Fig. 5. Eimac CD-8 planar structure, shown atop Tinkertoy module.

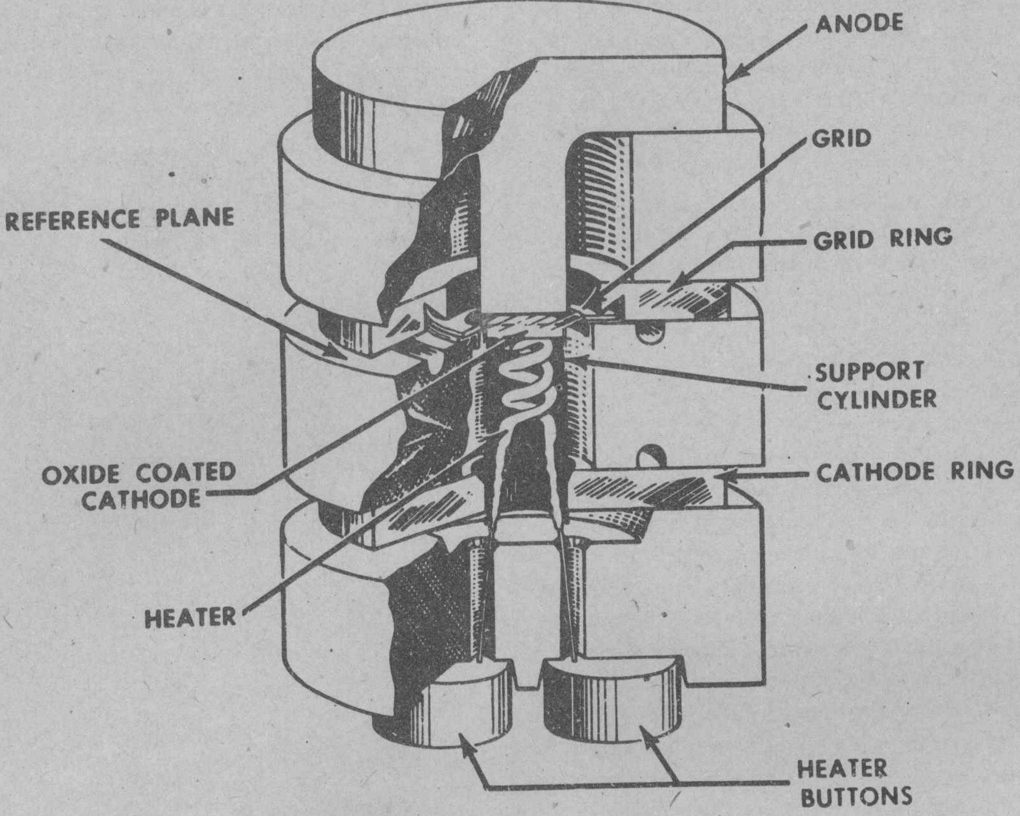


Fig. 6. General Electric 6844 (considerably enlarged).

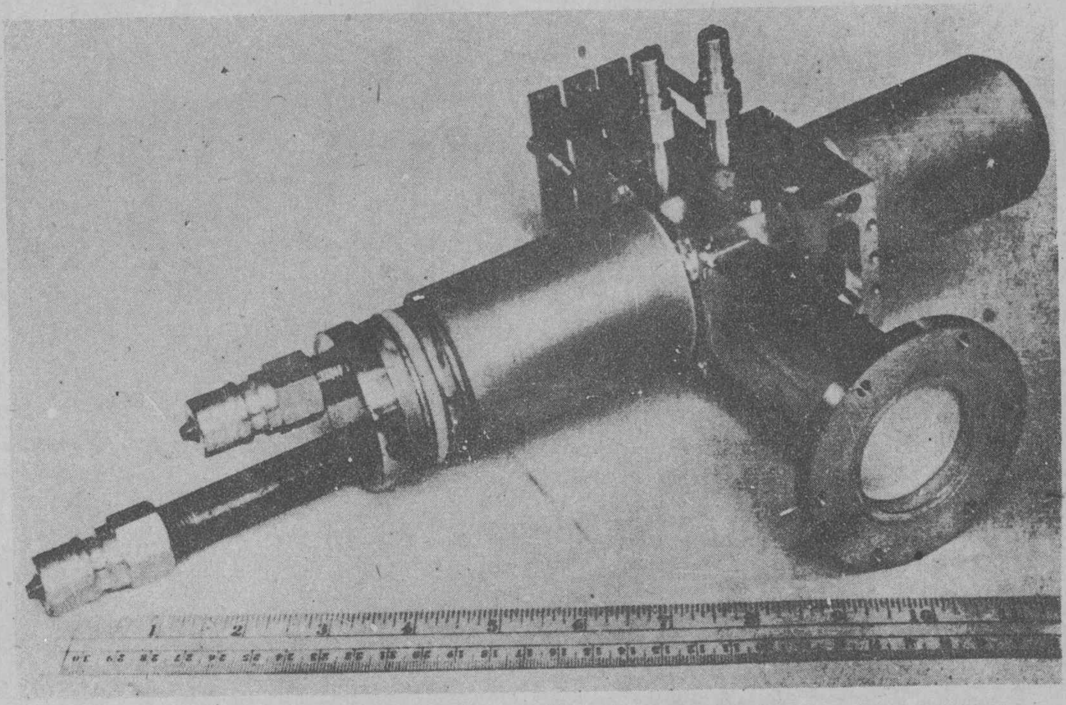


Fig. 7. Varian metal-ceramic klystron.

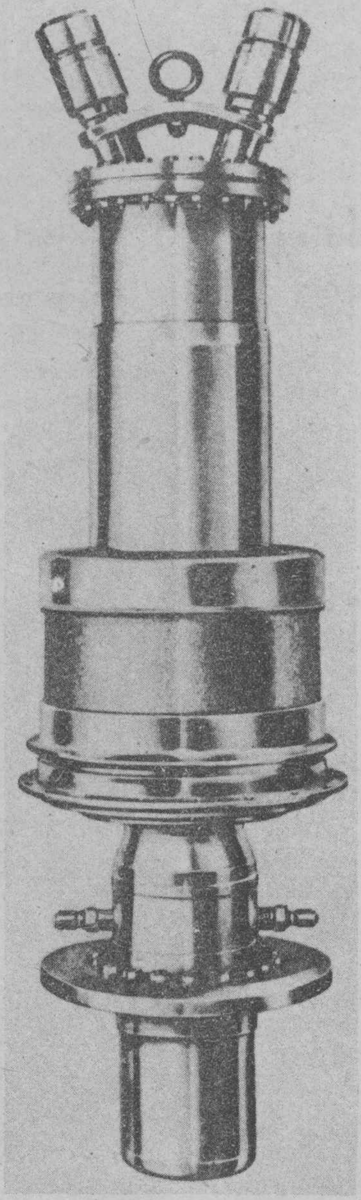


Fig. 8. RCA 2332A.

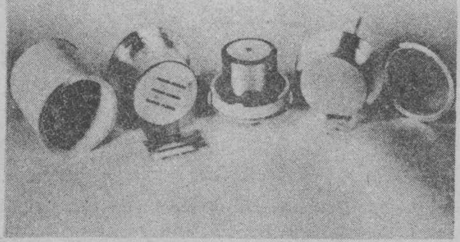


Fig. 9. Components of E.G.&G. developmental hydrogen thyratron.

2. Control of Alumina Bodies for Ceramic-to-Metal Seals

Frank J. Hynes
Raytheon Manufacturing Company

It is not the intention of this paper to discuss ceramic manufacturing in detail, but rather to point out a few methods of testing the suitability of various batches of alumina bodies for use in ceramic-to-metal seals.[1] The active-metal process, utilizing the hydrides of zirconium and titanium, tends to wet almost all ceramic materials, and thus no special sealing precautions are necessary. Our discussion will therefore be confined to methods of testing lots for use in the refractory metal process of sealing.

Before discussing these test methods, let us consider four ceramic parameters that affect fired ceramic alumina bodies:

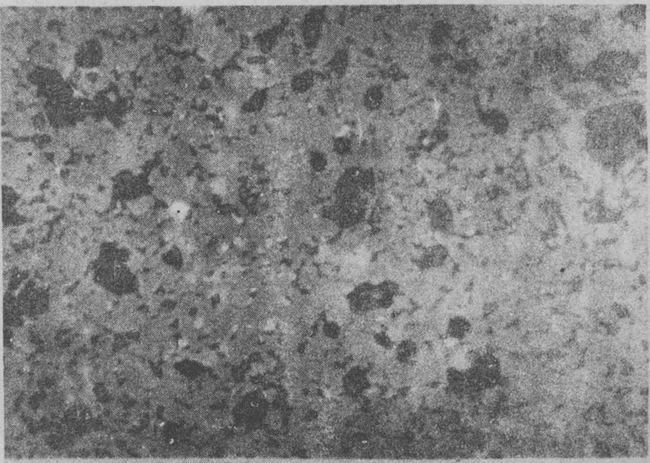
1. Chemical Formula. Generally, ceramic formulas are derived by varying two, three, or more fluxes with various alumina contents and processing through a particular manufacturing scheme. A particular formula is then selected which most nearly meets the particular chemical, physical, or electrical requirements. Navias[2] has shown some typical results of such investigations. Future lots depend on the reproducibility of the processing and on variations in the raw-material sources.

2. Particle Size and Particle-Size Distribution. These are generally controlled by keeping a close check on milling operations. Fine particles react at a lower temperature but tend to cause excessive shrinkage and firing warpage. For a particular scheme the coarsest graded size is generally preferable.

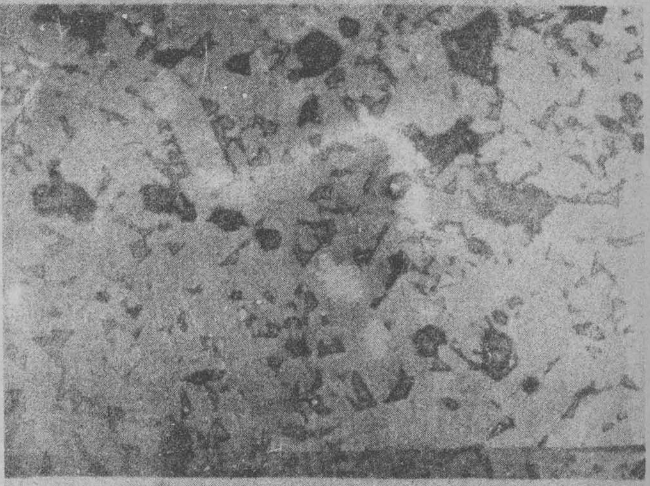
3. Forming. The method used depends on the particular shape desired and the equipment available. The method of forming affects the firing somewhat. For alumina bodies, hydrostatic pressing is highly favored. For a particular body, hydrostatically pressed parts will mature at cone 32½, extrusion will lower the maturing temperature about one cone, whereas casting will lower the firing temperature about 2 cones.

4. Firing Cycle. This presents one of the most difficult problems encountered in alumina production. Maturing can best be regulated by firing in small, closely controlled tunnel kilns.

At the recent ACS Convention, we[3] presented a paper showing the effect of firing temperature



Sample B-417. Fired 1550°C 4 hours.

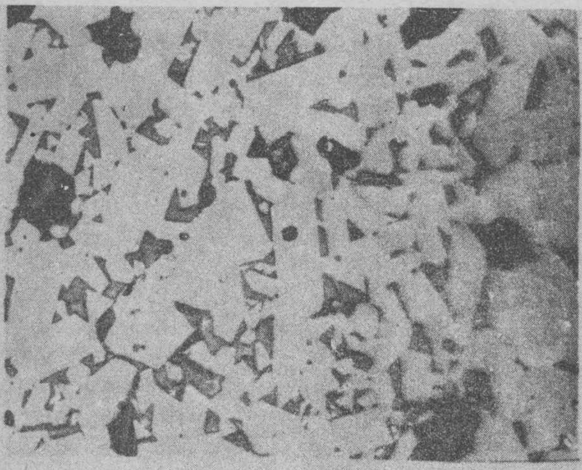


Sample B-406. Fired 1650°C 4 hours.

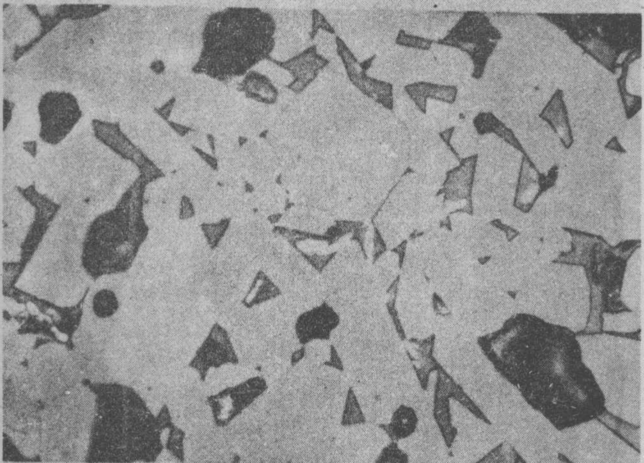
Fig. 1. Structure of alumina fired at 1550°C and 1650°C.

on various properties on a glass-bonded alumina body. A brief review of these data will aid in a discussion of controls. Figure 1 shows the structure of an alumina body at 1550°C and 1650°C. Figure 2 shows the structure at 1700 and 1750°C. Close observation of these figures will disclose three major points.

a) Alumina grains increase with firing temperature.
b) The void area varies approximately as specific gravity. In this instance the two end members have about 10 per cent voids and the other two have about 5 per cent voids.
c) The glass content increases with temperature.



Sample B-421. Fired 1700°C 4 hours.



Sample B-414. Fired 1750°C 4 hours.

Fig. 2. Structure of alumina fired at 1700°C and 1750°C.

Many investigators, such as Williams,[4] Nolte, Spurck,[5] Cronin, Hynes, and Schuck[6] have described various methods of making refractory metal seals. Bender[7] has described the effect of particle size and Pincus[8] has proposed the use of oxides in the metalization. From these data and from operating experience, it is apparent that the following variables should be kept constant if one is to test various lots of alumina bodies for acceptability:

1. Particle size of various metal powders.
2. Degree of mixing of moly and other additives.
3. Method of application and thickness of fired-on layers.
4. Time-temperature relations in atmosphere metalizing furnaces.
5. Mechanical design of seal and brazing fixtures.
6. Atmospheres and dew points of firing and brazing cycles.
7. Brazing conditions.

Into this complicated process one must continually inject new lots of ceramic materials with their accumulative variables.

Initially we found it advisable to check various batches for sealing qualities before time was invested in diamond grinding to specifications. At this time it was also convenient to make other mechanical, chemical, and electrical tests.

Before describing specific tests it might be well to point out how some of these ceramic properties may vary. Figure 3 will show how these properties vary with firing temperature.

This figure shows how specific gravity, porosity, and modulus of rupture vary with firing temperature. Note how both the modulus of rupture and specific gravity rise to reach a maximum and then fall off. Also note that the modulus of rupture reaches a maximum slightly before specific gravity. The ceramist would call this particular body overfired at any temperature over 1650°C.

Figure 4 portrays impact resistance, loss factor, and ceramic-to-metal seal strength plotted against firing temperature. The ceramic-to-metal seal strength is measured by a method described by Cronin.[9]

The following have been found to be practical control measures:

Visual Observations

All parts should be inspected for mechanical flaws. Particular emphasis should be placed on spherical crystalization,[10] contamination, and other inhomogeneities at two points before and after firing at normal metalizing temperatures. Firing in "dry" reducing atmospheres tends to bring out defects more readily than firing in wet atmospheres. Defects such as shrinkage, blisters, weight loss, and warpage will also be detected by these simple procedures.

Physical Tests

Apparent specific gravity is a simple test which can be quickly and accurately made. We have fairly well correlated specific gravity with bond tests for our body and sealing practices. It is a simple matter to decide on which side of the maximum the piece is by observation under reflected light. Remembering the grain growth shown in Figs. 1 and 2, comparison then can be made by eye to known standards.

A strength measurement on sealing test pieces will provide data to correlate with specific gravity determinations, and also will tend to show possible mechanical flaws. These modulus-of-rupture determinations can be made after hydrogen firing, if desired; warpage, however slight, will affect the results. It is well to use caution in making comparisons between pieces before and after hydrogen-firing. One reason is that conditions in the metallizing cycle will likely lead to a quenched condition. Rutgers[11] has shown that the strength of alumina bodies can be improved by quenching techniques. Also, if one does not know the ceramic history of the piece, it may be impossible to predict an expected increase or decrease in strength.

Sealing Tests

Comparison of bond tests with production yields has shown that high values of bond give low scrap factors. Some seal assemblies, such as thin windows, may require higher bond values. An arbitrary limit may be set at 2000 lb. below which parts are not accepted. Values of the order of 2500 to 3000 are normally encountered.

In addition to the bond test, a use test is also performed. Ceramic assemblies for tube structures usually require subsequent heating cycles. Before any number of parts for a particular seal are accepted, six assemblies are made. These vacuum-tight assemblies are then passed through a continuous belt conveyor operating at 800°C. If the assemblies remain vacuum-tight after six passes, the remainder of the lot is accepted.

Electrical Tests

No electrical tests are made once a particular processing schedule has been established. Our experience has been that the tests outlined above are satisfactory.

We have briefly described how some complicated variables of ceramic manufacturing and sealing processes can be dealt with to give high production yields, even though it is difficult to achieve optimum electrical, physical, and chemical characteristics at the same time. In any case, high seal strength is a primary consideration.

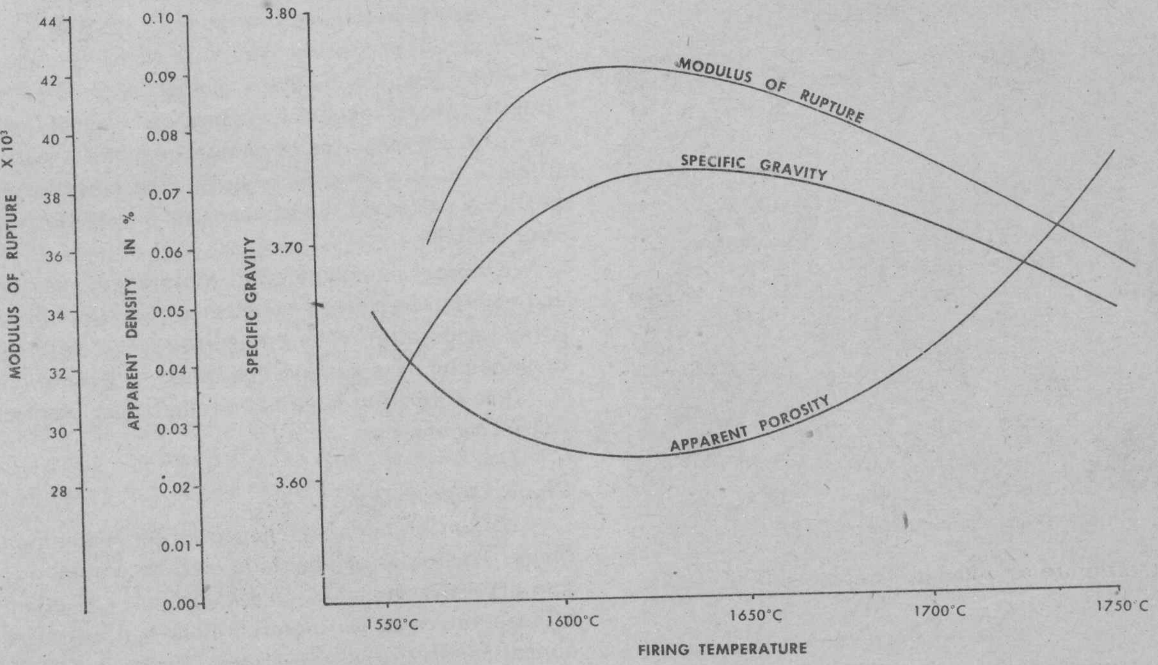


Fig. 3. Variation of rupture modulus, density, and porosity with alumina firing temperature.