

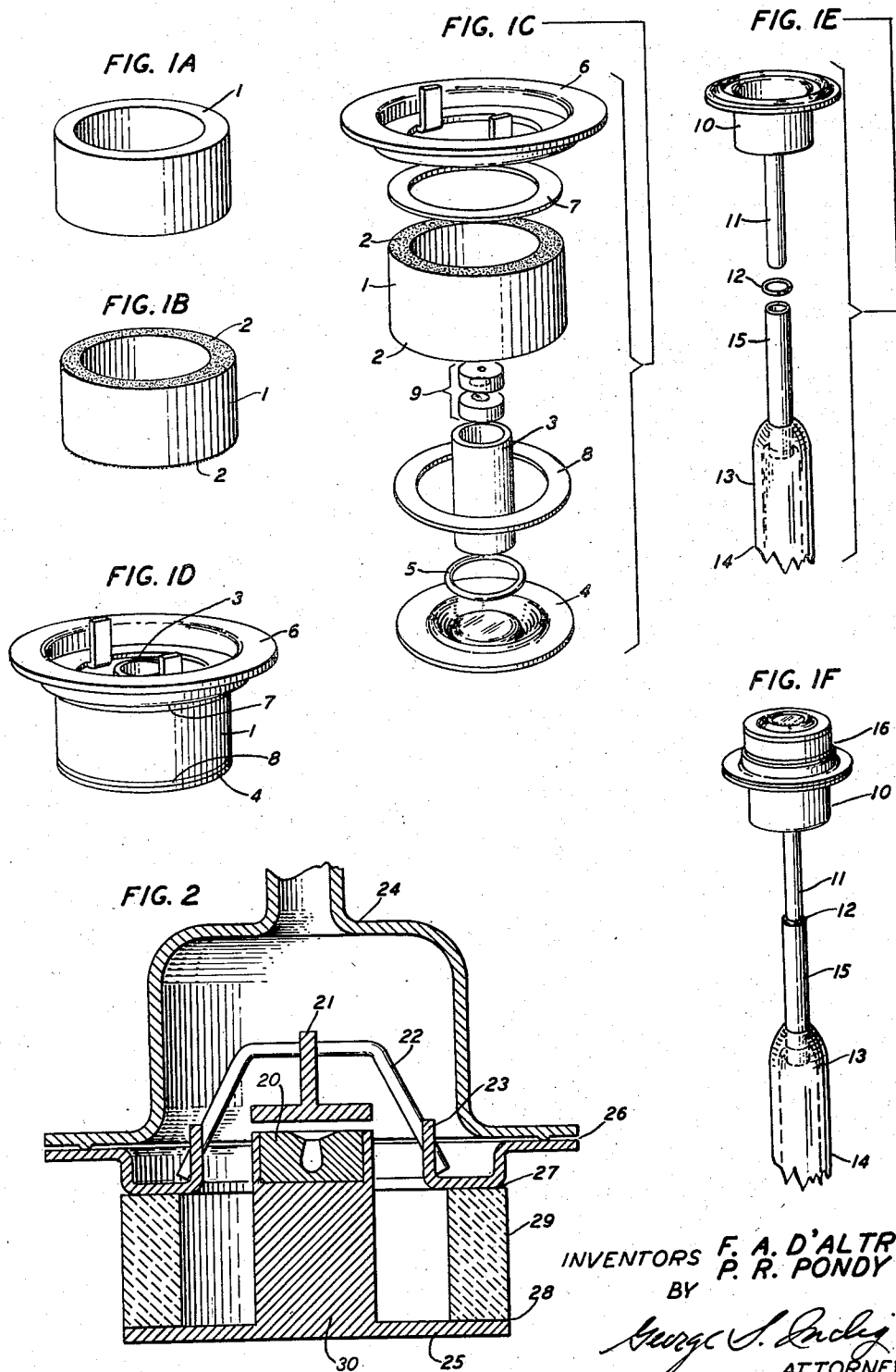
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GAS SEAL

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1

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GAS SEAL

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This invention relates to a gas-tight ceramic-to-metal seal. The seal of this invention is particularly applicable to gas and vacuum electron tube structures.

In the electron tube art and in the manufacture of precision electrical devices in general, where a controlled atmosphere or vacuum is desirable, it is frequently necessary to produce gas-tight seals between components which may be made of dissimilar materials. A considerable amount of research and development time has been devoted to developing sealing techniques adequate for such purpose.

The desirability of ceramic details due to their refractory nature and excellent dielectric properties and the requirement of metal conducting parts in electrical devices have resulted in a considerable amount of development time being directed to sealing these materials one to the other. The first phase of this development program was directed to the design of metallic alloy materials of the requisite refractory nature and having temperature coefficients of expansion making them compatible with the desirable ceramic compositions. This resulted in the development of Kovar and similar compositions.

Several years ago it was determined that an effective gas-tight seal could be made between Kovar and various ceramic compositions by a two-step process including the application of a metallizing layer to the ceramic surface to be bonded, followed by the application of a brazing material which joined the metallic surface to the metallized ceramic. Such bonds, which frequently utilize a molybdenum-manganese or molybdenum-iron metallizing layer and a brazing material such as an alloy of silver and copper, are in common use in the electron tube industry today. In general, bonds of this type made between compatible materials have the requisite physical properties and result in electron tube and other electrical structures suitable for most common usage. A particular advantage of such bonds resides in their refractory nature, which permits degassing operations at temperatures of the order of up to 600° C., thereby permitting removal of most gaseous contaminants which might otherwise impair the operating characteristics of the device.

With the continuing developments of advanced tube structures having closer tolerances, and with the design of more complex electronic circuits requiring a greater degree of stability in circuit components, it has become increasingly apparent that conventional ceramic-to-metal seals, once adequate, are now serving to limit the operating characteristics of such devices. It has been recognized that this limitation could, in part, be obviated by higher degassing temperatures, permitting more complete removal of contaminants. In general, attempts to degas or otherwise process such sealed devices at temperatures in excess of 600° C. have resulted in contamination by elements contained in the metallizing or brazing materials of the seal. Accordingly, use of such a seal containing the common copper-silver alloy or other similar materials results in a discernible coating of one or another

2

of the ingredients of such braze on the cathode or other element contained in the device to be sealed, thereby affecting the electrical characteristics of the device.

In accordance with this invention there has been developed a ceramic-to-metal seal and method of applying such seal which, in large part, overcomes the deficiencies of the common seals used in electron tube and other structures. This seal, which utilizes a metallized layer produced by application of molybdenum or tungsten to which titanium or zirconium may be added, the latter generally produced upon thermal decomposition of the corresponding hydride, and a brazing layer consisting of a palladium-nickel or palladium-cobalt alloy, desirably of a comparatively low melting composition in accordance with the composition diagram of those two materials, permits degassing and other high temperature processing at temperatures of the order of 1000° C. Gas diode structures, sealed in accordance with the instant invention, manifest sustained voltages extremely close to the inherent characteristics of the cathode materials themselves.

The inventive seal and process are described in conjunction with the following figures, in which:

Figs. 1a through 1f are perspective views of tube components and a tube structure depicting various stages of manufacture of a device utilizing the inventive process described herein; and

Fig. 2 is a cross section elevational view of a tube structure utilizing a ceramic-to-metal seal of this invention.

With further reference to Figs. 1a through 1f, Fig. 1a depicts a ceramic body 1 to be bonded. Ceramic materials suitable for the instant processes and seal should have a softening point above the brazing temperatures of the brazed material to be used in the seal (from 1300–1400° C.) and are generally aluminum oxide containing. Examples of suitable ceramic materials will be discussed herein. These include such materials as alumina, zircon, fosterite and steatite.

In accordance with Fig. 1b, ceramic body 1 has been metallized on both flat surfaces. The metallizing layer 2 may consist of a mixture of molybdenum and titanium produced by spraying the surface with, for example, a 95–5 weight percent mixture of elemental molybdenum and titanium hydride, followed by sintering at a temperature of the order of 1560–1600° C. in a manner to be described.

In accordance with Fig. 1c, there are shown cathode holder 3, which may be made of molybdenum, base plate 4, which may be made of Kovar or other material having suitable refractory and physical properties, brazing ring 5, desirably made of a palladium-nickel alloy, to be used for bonding holder 3 to base plate 4, top plate 6, which may be made of Kovar, and brazing washer 7, which in accordance with this invention is constructed of palladium-nickel or palladium-cobalt to be used for bonding top plate 6 to the uppermost metallized surface 2 of ceramic body 1. Base plate 4 is bonded to lower metallized surface 2 of ceramic body 1 through brazing washer 8 which may be made of the same material as washer 7. This view also shows hollow niobium cathode elements 9 to be secured in holder 3 by means of crimping after the seals have been made.

Fig. 1d depicts the structure after bonding of the elements shown in Fig. 1c. There is here shown ceramic body 1 having metallized surfaces 2, having top plate 6 bonded thereto on its uppermost surface through brazing layer 7, and having bottom plate 4 attached to the lowermost metallized surface 2 of ceramic body 1 through palladium-nickel brazing layer 8. The structure shown is completed by molybdenum cathode holder 3 attached

to base plate 4 by means of palladium-nickel brazing ring 5.

In accordance with view 1e, there are shown Kovar cap 10 provided with tubulation 11, solder ring 12, which may be made of palladium-nickel, and tubulation 13, consisting of glass tube 14 and Kovar tube 15, the latter to be sealed to tube member 11 of cap 10.

In accordance with view 1f, cap 10 has been bonded to the tube structure of view 1d. These two parts may be joined by conventional resistance welding means. Tubulation 13 is shown sealed to tube structure 11 of cap 10 by means of brazing layer 12.

In accordance with conventional means, tubulation 13 is attached to a pumping means, not shown, the entire tube structure 16 is heated to the desired degassing temperature, and pumping is commenced. After degassing is completed, tube 16 is filled with a gaseous atmosphere such as neon-helium and is then sealed off from tube 13. This completes the tube.

Fig. 2 depicts a gas tube diode structure similar to that produced in accordance with the process of Figs. 1a through 1f. This structure consists of hollow cathode 20, which may be made of niobium or other suitable cathode material contained in molybdenum holder 30, plate 21, which may be made of zirconium or other suitable material, the latter supported in fixed position relative to cathode 20 by structural member 22, which may be made of molybdenum, and welding tabs 23, which may conveniently be made of Kovar. The cathode and anode elements are enclosed within cap 24, which may be Kovar, ceramic member 29, and Kovar bottom plate 25, which latter is part of the cathode structure. Conventional resistance weld 26 and metallized braze seals 27 and 28 result in a gas-tight structure. Seals 27 and 28 are composite seals consisting of a molybdenum-titanium metallizing layer on the bonded surfaces of ceramic member 29 and a palladium-nickel or palladium-cobalt brazing layer in intimate contact with both the metallized and Kovar surfaces, which are bonded.

The general procedure to be followed in producing the ceramic-to-metal seal of this invention is set forth below. The ceramic surface to be bonded is first coated with the components which produce metallizing. Application of these materials may be by spraying, by silk screen technique, by painting, or by any other suitable means. In accordance with conventional procedure, these materials are applied in a carrier, such carrier, which may be a nitrocellulose-amyl acetate mixture, to be suitable should be decomposable to gaseous components which leave the system prior to sintering. These materials should leave no carbonaceous or other residue.

It is a general requirement of the metallizing ingredients that the resultant layer be thermally compatible with the brazing material (palladium-nickel or palladium-cobalt); that it have sufficiently low volatility at the highest temperatures to be attained during processing or operation of the final structure; that it have a low reactivity with respect to the ceramic material to be bonded at processing and operating temperatures; and that it have sufficient penetration in the ceramic to form a good bond. In general, many metallizing materials which have found use heretofore are unsuitable in this process for one or another of the above reasons, chiefly because of the higher processing temperatures (up to about 1000° C.) to be used. For this reason, molybdenum-manganese compositions, which are incompatible with the brazing materials herein, and titanium hydride, which may form a low temperature eutectic with the nickel component in the Kovar element to be bonded, may not be used. Materials which have been found suitable include elemental molybdenum, mixtures of molybdenum and titanium hydride containing up to 10 weight percent of the hydride and similar mixtures in which tungsten and/or zirconium hydride is substituted for the molybdenum or titanium hydride.

Suitable ceramic materials must be capable of withstanding the higher brazing temperatures used in this process. For this reason, such ceramic materials having softening points below about 1400° C. are unsuitable. The best known ceramic materials having the requisite softening points are based on the aluminum oxide system. Such aluminum oxide ceramics to be useful should have a purity range of from about 90% to about 99%. Purer materials do not appear to adhere properly to the metallized bond. Less pure materials may have a softening point below the brazing temperature of the process, generally resulting from the larger inclusion of silica. Ceramic materials meeting the above requirements include alumina, zircon, fosterite and steatite. Commercial materials which have been used in preferred embodiments herein are: "Coors, AI-200," "Almonox 4462" and "Diamonite," made by Coors Porcelain Company, Golden, Colorado, Frenchtown Porcelain, Frenchtown, New Jersey, and U.S. Ceramic Tile Company, Canton, Ohio, respectively. All of these materials contain of the order of 95 weight percent of aluminum oxide, the remainder primarily silica. The temperature coefficient of expansion of such ceramic materials is typically of the order of 8.3×10^{-6} cm./cm./°C. at 600° C.

The sprayed or otherwise deposited surface is next sintered. Sintering may be carried out over a temperature range of from about 1550° C. to about 1600° C. for a period of from about 5-60 minutes. The specific examples herein were produced by sintering for 30 minutes. In general, sintering at temperatures higher than the indicated maximum results in devitrification. As is well known in the art, this upper limit may be slightly extended for certain of the materials in the described class. Although sintering may be effectively carried out at temperatures below 1550° C., the sintering time must be extended. This lower limit is chosen in accordance with conventional practice in which sintering is carried out at about two-thirds of the melting point of the predominant metallizing component.

Sintering is carried out in wet hydrogen or wet forming gas, desirably of a dew point of +20+5° C. The dew point of the atmospheric gas should be kept between the limits of +10° C. and +30° C. Below the minimum it is found that the gas is too reducing, thereby impairing wetting of the ceramic by the metallized layer. Above a dew point of +30° C. the atmosphere becomes oxidizing with respect to the molybdenum-titanium mixture, thereby also impairing wetting.

After metallizing, bonding to the metallic surface is brought about by use of a brazing material. In accordance with this, the brazing material is either an alloy of palladium-nickel or palladium-cobalt. The composition of the brazing material is not critical except with respect to the brazing temperature which may be tolerated by the other tube components present during this step. Since a lower brazing temperature for either of the brazing compositions designated does not in any way impair the operating characteristics of the tube, it is generally desirable to choose a lower melting composition of either system in accordance with their composition diagrams. In general, since the Kovar elements to be included have a melting point of about 1450° C., any brazing alloy having a melting point at or below about 1400° C. is suitable. Substitution of platinum or other higher melting metallic components raises this limit. For the palladium-nickel system a 1400° C. maximum indicates a range of from 80-20 to 10-90 palladium-nickel, with the lowest melting composition occurring at about 60-40+5%; for palladium-cobalt the included range is from 12-88 to 92-8 palladium-cobalt, with the lowest melting composition occurring at about 65-35 (all compositions based on weight percent).

The brazing material may be applied in the form of

a powder or a solid body such as a washer, wire or other configuration. A slight compressive force being desirable to effect intimate contact, the metallized ceramic, brazing material and metallic body to be bonded thereto are generally brazed in a jig.

The jig is next placed in an oven which is maintained at the brazing temperature of the chosen material. Although the oven temperature may exceed the brazing temperature, it should not be higher than either the softening point of the ceramic or the melting point of the metallic body. Heating is carried out in a wet hydrogen or wet forming gas atmosphere as described above. Time of heating is not critical, a range of from 5 minutes to 60 minutes having been found suitable.

After brazing is completed, the jigged structure is gradually cooled to avoid thermal shock. Cooling is carried out in the same atmosphere of wet hydrogen or wet forming gas. Minimum cooling time is dependent upon the dimensions of the structure. For the structure shown in Fig. 1d, of overall dimensions of the order of $\frac{1}{4}$ " by $\frac{1}{16}$ " in diameter, a cooling time of the order of 15 minutes to cool the structure from the melting point of 60–40 palladium-nickel (1227–1237° C.) to room temperature has been found suitable.

Subsequent processing steps in the manufacturing of a tube structure are well known to those skilled in the art and are not detailed here. Tube structures made in the above manner have been found to be vacuum-tight by conventional leak detection methods carried out under vacuum of the order of 10^{-7} millimeters of mercury. Such structures have been outgassed at temperatures as high as 1000° C. to 1050° C. under vacuum of the order of 10^{-6} millimeters of mercury. The avoidance of contamination in structures so produced is evidenced by visual inspection as compared, for example, with the copper deposit left by use of 73–27 copper-nickel brazing material and by manifestation of sustained voltages almost identical with those inherent for the cathode material and structure used.

The above general description is in terms of metallic structural elements made of Kovar, which is an alloy of iron, nickel, cobalt and manganese of weight percent composition of approximately 53.7–29–17–3. This material has a temperature coefficient of expansion of approximately 8×10^{-6} at 600° C. and exactly matches Coors AI-200 ceramic at 700° C. Other materials such as platinum having suitable expansion coefficients may, of course, be substituted for Kovar. Other variations in the general procedures outlined above are known to those skilled in the art. A description of such alternate procedures is seen in "Ceramic Age," February and September 1954.

The following specific examples are directed to the manufacture of ceramic-to-metal seals, the first utilizing a palladium-nickel brazing material, the second utilizing palladium-cobalt. Both examples relate to the making of such seals in a talking path gas diode of the type depicted in Fig. 2. The manufacturing steps necessary to the making of the final structure once the seal has been made are considered to be outside the scope of this specification. Such procedures are well known to those skilled in the tube manufacturing art. The operating characteristics of the tubes are briefly discussed only in terms of sustained voltage, that is, the minimum voltage required to maintain a constant current flow between cathode and anode. This characteristic is considered to be of significance since comparison of it with the same characteristic observed in the identical structure in a wholly glass envelope indicates the degree of or lack of contamination of cathode and anode elements produced on degassing and any other high temperature process. As is seen, the sustained voltages for the metal-to-ceramic as compared with that for the glass structure are almost identical, indicating a virtual absence of contamination. Other characteristics of the final tube structures were

in all respects those expected for the described configuration.

Example 1

A Coors AI-200 ceramic (95% aluminum oxide ceramic manufactured by Coors Porcelain Company) ring of approximate dimensions 150 mills x 275 mills I.D. by 375 mills O.D. was coated with a 95–5 weight percent mixture of elemental molybdenum and titanium hydride powders by spraying to a thickness of about 0.002" on both flat surfaces. The ceramic ring so coated was then sintered in an alundum core-type furnace at a temperature of 1550° C. $\pm 20^\circ$ C. for a period of 30 minutes in an atmosphere of wet hydrogen having a dew point of $+20^\circ$ C. $\pm 5^\circ$ C. The ceramic ring so metallized was placed in a jig with two rings of 60–40 palladium-nickel of a thickness of .003" and Kovar details to be joined thereto (details 4 and 6 of Fig. 1c). The jig was placed under slight compression, the assembly was placed in a nickel boat which was pushed into an oven maintained at 1275° C. $\pm 10^\circ$ C. having a moving atmosphere of wet forming gas of a $+20^\circ$ C. $\pm 5^\circ$ C. dew point. The assembly was left in the oven at the said temperature for a period of about 15 minutes, after which the boat was gradually moved into successively cooler zones in the furnace at the rate of about one-half inch per minute, resulting in attainment of room temperature in a period of about 15 minutes. The seal so produced was determined to be vacuum-tight at a vacuum of 10^{-7} millimeters of mercury in an atmosphere of helium on a mass spectrometer. The tube structure was then completed in the general manner depicted in Figs. 1a through 1f, and was outgassed in a vacuum of about 10^{-6} millimeters of mercury at a temperature of about 1025° C., local heating being produced by an R. F. furnace. The tube structure was then filled with an atmosphere of helium and neon gas. The resultant structure resembling that shown in Fig. 2 had a sustained voltage of 98.7 ± 0.5 volts. This value was compared with the sustained voltage measured on the same structure contained in a sealed glass tube, which latter was found to be 98.8 ± 0.5 volts.

Example 2

A Coors AI-200 ceramic ring of the same approximate dimensions as in Example 1 was coated with a 95–5 weight percent mixture of elemental molybdenum and titanium hydride powders by spraying to a thickness of about 0.002" on both flat surfaces. The ceramic ring so coated was then sintered at a temperature of 1550° C. $\pm 20^\circ$ C. for a period of 30 minutes in an atmosphere of wet hydrogen having a dew point of $+20^\circ$ C. $\pm 5^\circ$ C. The ceramic ring so metallized was placed in a jig with two rings of 65–35 palladium-cobalt of a thickness of .003" and Kovar details to be joined thereto (details 4 and 6 of Fig. 1c). The jig was held under slight compression, the assembly was placed in a nickel boat which was pushed into an oven maintained at 1265° C. $\pm 10^\circ$ C. having a moving atmosphere of wet forming gas of a $+20 \pm 5^\circ$ C. dew point. The assembly was left in the oven at the said temperature for a period of about 15 minutes, after which the boat was gradually moved into successively cooler zones in the furnace at the rate of about one-half inch per minute, resulting in attainment of room temperature in a period of about 15 minutes. The seal so produced was determined to be vacuum-tight at a vacuum of 10^{-7} millimeters of mercury in an atmosphere of helium on a mass spectrometer. The tube structure was then completed in the general manner depicted in Figs. 1a through 1f, and was outgassed at a vacuum of about 10^{-6} millimeters of mercury at a temperature of about 1025° C., local heating being produced by an R.F. furnace. A tube was then filled with an atmosphere of helium and neon. The resultant structure resembling that shown in Fig. 2 had a sustained voltage of 98.7 ± 0.5 volts. This value was compared with the sustained voltage measured on the same structure contained in a sealed glass tube, which latter was found to be 98.8 ± 0.5 volts,

The cathode material used in the tube structures in accordance with Examples 1 and 2 was niobium.

The seal and process of this invention were developed primarily for use in electron tube structures. For this reason the above description is primarily in such terms. It is well known, however, that ceramic-to-metal seals are required in other types of structures. Wherever it is desirable to make such a seal, to subsequently process a structure containing such a seal, or to operate such structure, at temperatures substantially above the order of 600° C., the seal and process of this invention may be used to advantage. Certain processing steps and conditions have been described in specific terms. It is intended that these be considered as exemplary only and that the claimed invention not be so limited.

What is claimed is:

1. A gas-tight ceramic-to-metal seal comprising successively a ceramic surface, a metallizing layer comprising at least one metal selected from the group consisting of molybdenum and tungsten, together with up to 10 weight percent of at least one metal selected from the group consisting of titanium and zirconium, a brazing

material comprising palladium together with at least one metal selected from the group consisting of nickel and cobalt, and a metallic surface.

2. The gas-tight seal of claim 1 in which the ceramic body is aluminum oxide of a purity of between 90% and 99% by weight and in which the said metallic surface is an alloy of the approximate composition expressed in weight percent 53.7% iron, 29% nickel, 17% cobalt, 0.3% manganese.

3. The seal of claim 2 in which the brazing material is palladium-nickel of approximate weight composition 60-40%.

4. The seal of claim 2 in which the brazing material is palladium-cobalt of approximate weight composition 65-35%.

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