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FABRICATION OF METAL TO CERAMIC SEALS

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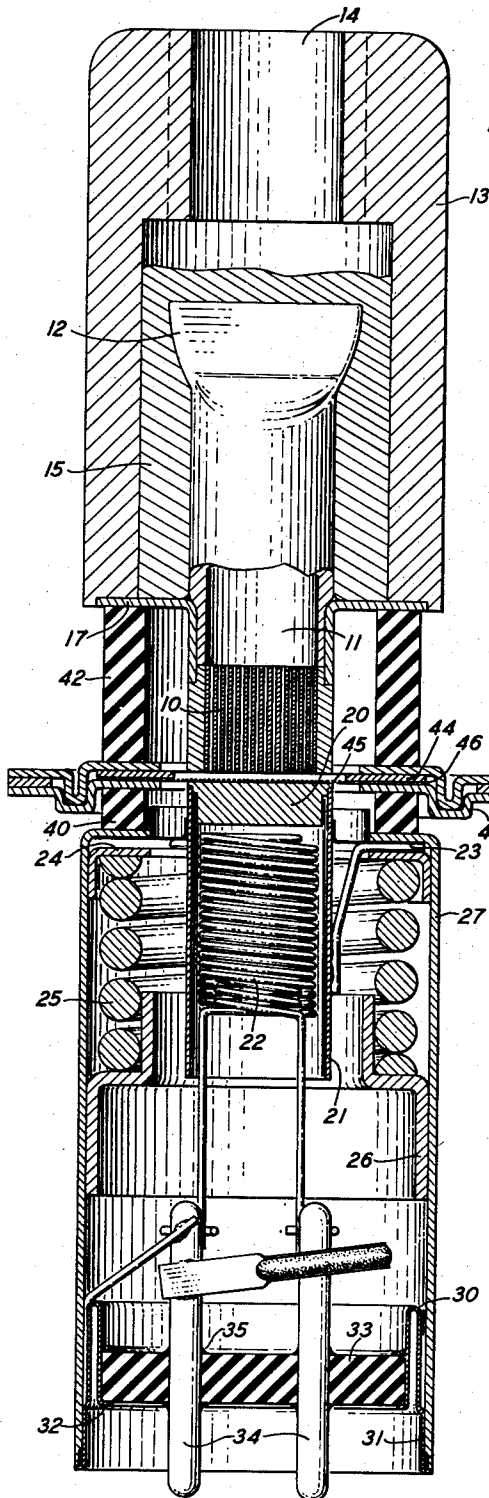


FIG. 1

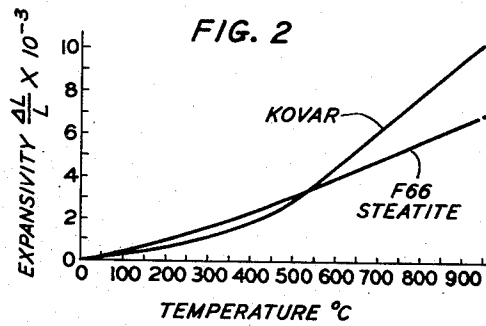
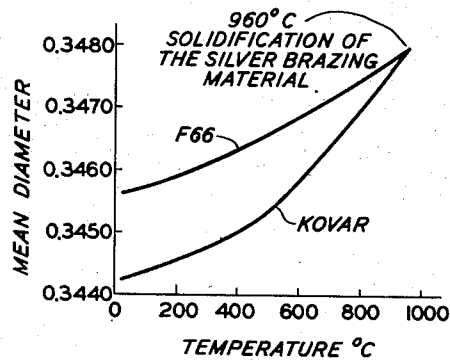


FIG. 3
COOLING CHARACTERISTIC OF
STEATITE-KOVAR LAP-TYPE SEAL



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2,708,787

FABRICATION OF METAL TO CERAMIC SEALS

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5 Claims. (Cl. 29—473.1)

This invention relates to metal to ceramic seals and particularly to the fabrication of such seals for electron discharge devices.

Various advantages have been known for employing ceramics rather than glass in the envelope of electron discharge devices, but the difficulties in obtaining vacuum tight ceramic to metal seals have generally prevented the employment of ceramic materials. Certain of these advantages are the better dielectric properties whereby less loss is introduced into high or microwave frequency tubes and the facility with which the dimensions of ceramic parts may be extremely accurately maintained within precise limits. This latter is also particularly of advantage in microwave tubes wherein the electrode structure or a part thereof is itself a portion of the circuit so that variations in the size of the insulator portions of the envelope cause different natural frequencies.

A further great advantage of employing ceramic insulating parts rather than glass parts in vacuum tube envelopes is the avoidance of introducing any oxidation in the device. In glass to metal seals oxidation occurs in order to achieve a good seal and subsequent chemical cleaning is never complete in removing from the device the oxidation.

Because of their dielectric and other properties the ceramics generally known as steatites lend themselves to incorporation in electron discharge devices. Certain of these ceramic materials are disclosed in M. D. Rigerink Patent 2,332,343, issued October 19, 1943. Because of their high direct current resistance, low electrical losses at high frequencies, mechanical strength and freedom from brittleness, and ease of manufacture, these materials lend themselves to incorporation in electron discharge devices. Example 1 in the above-mentioned patent, which material has become known as F66 steatite and shall be so referred to herein, has particular thermal qualities which recommend it for employment in electron discharge devices. Specifically these characteristics include a uniform coefficient of thermal expansion, as certain steatites and other ceramics have marked inflections in the coefficient when plotted against temperature, a low coefficient of thermal expansion and thus a higher resistance to thermal shock than usually found in such ceramics, and a thermal expansion that approximates that of the particular metal that has been found to be most desirable for employment in electron discharge devices, a nickel-iron-cobalt alloy metal known commercially as "Kovar" by which name it will be referred to herein. The composition of this alloy is 29 per cent nickel, 17 per cent cobalt, about 0.2 per cent manganese and the remainder iron.

There are also a number of metals which could be employed in seals in electron discharge devices but each has one or more deficiencies when compared with Kovar. The requirements placed upon the metal are that it can be worked into various shapes, will not easily oxidize or be attacked by hydrogen or nitrogen, can be subjected to high temperatures, can be made with a high degree of precision, and of course be relatively inexpensive. Thus

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molybdenum, which is much employed in vacuum tubes, is difficult to work or form parts and oxidizes in air at 400° C. and higher. Tantalum is attacked by hydrogen and nitrogen. Columbium might be considered but it is a rare metal and also will form hydrides and nitrides at high temperatures. These factors and the fact that the coefficient of expansion of Kovar is accurately controlled during the manufacturing of the alloy, as it was developed to match the thermal coefficient of certain glasses, have led to a wide acceptance of the material in the vacuum tube and electron discharge device field.

These considerations therefore suggest that the envelope of the device should be composed of Kovar and a steatite having a thermal coefficient of expansion substantially matching that of Kovar, or more particularly of F66 steatite. However, it is also desirable that the parts be lap or butt sealed. Prior ceramic to metal seals have generally been of the ring type wherein the material having the larger expansivity is placed outside the other so that on cooling it will compress the other material and thus insure a seal. Ring type seals require very fine tolerances on the diameters of the ring parts being joined, which tolerances are very difficult to maintain. However, in certain applications, and particularly for employment in high frequency, as microwave, electron discharge devices, such a seal is inapplicable and it becomes important to have butt seals.

It is therefore an object of this invention to enable the fabrication of butt type metal to ceramic seals and particularly such seals capable of employment in vacuum apparatus, such as electron discharge devices, where exceedingly close spacings are required. More specifically it is an object of this invention to enable the successful fabrication of vacuum tight butt seals between Kovar and F66 steatite.

In our studies of ceramic to metal seals we have discovered that it is possible to produce one or a very few vacuum tight seals out of a large number of attempts by trying various materials and various procedures. However, none of these resulted consistently in successful vacuum tight seals, even though an occasional operative seal might result, as there was no certainty as to the outcome and a high probability that the seal would be a failure. We have been able to successfully construct, on a production basis, large numbers of seals with only a small allowance for rejected seals, as is normal in manufacturing and including rejects for other reasons than failure of the seal itself, in accordance with our invention. The failure of prior seals has been obviated by our discovery that the various steps involved in the process of fabricating the seals are critical and that deviations from prescribed standards may prevent the successful fabrication of such seals.

One specific procedure in accordance with our invention whereby the successful production of seals between Kovar and a steatite having a thermal coefficient of expansion substantially matching that of Kovar, such as F66 steatite, is attained comprises the following steps: A molybdenum-iron suspension of very fine particles is sprayed onto the surface of the steatite, the thickness of the sprayed layer being just sufficient to cover the surface. When the particles are of from 5 to 8 micron size the layer is from 0.0006 to 0.0008 inch thick. The steatite member is then heated up to a temperature from 10 to 15° C. below the maturing temperature of the ceramic for twenty minutes in an atmosphere of wet forming gas. A nickel layer is next sprayed onto the surface, the thickness of the layer being again just sufficient to cover the metallized surface. With a four micron particle size nickel the layer should be a minimum of 0.0006 inch thick. The nickel is then sintered by heating, as in a hydrogen atmosphere at 1100° C. The seal is made be-

tween this metallized steatite surface and a copper flashed Kovar surface by interposing therebetween a silver washer, the volume of silver being equivalent to a one mil washer over the whole area of the seal, and heating the seal at a maximum temperature of 1000° C. for ten minutes. None of the rates of heating or cooling involved should exceed 50° C. per minute.

The criticalness of these steps and the reasons why such fine control is a prerequisite to the successful fabrication of steatite-Kovar seals can be best understood by reference to the following detailed description and the accompanying drawing, in which:

Fig. 1 is a cross-sectional view of one illustrative electron discharge device utilizing a steatite-Kovar envelope and specifically seals between Kovar and F66 steatite members fabricated in accordance with one specific embodiment of this invention;

Fig. 2 is a graph of the thermal coefficient of expansion with temperature for Kovar and F66 steatite; and

Fig. 3 is a graph of mean diameter of the Kovar and steatite members of the envelope of the device of Fig. 1 plotted against temperature.

Referring now to the drawing, Fig. 1 shows a microwave triode in which this invention is employed. This specific triode comprises a honeycomb anode 10 to which is directly attached an exhaust tubulation 11 which has a closed end 12 sealing the tubulation. A protective cap 13 surrounds the anode, the cap having a threaded aperture 14 at its end to facilitate connection to the plate. A solder 15, which may be of a tin, lead, silver mixture, covers the closed end 12 of the anode tubulation 11. The cap 13 and solder 15 both serve to protect the closed end 12 of the exhaust tubulation 11 from damage due to mishandling causing physical shock or impact on the tube. However, if the threaded aperture 14 is employed for connection to an air cooling system the solder 15 may be omitted. The anode is supported by an anode connector ring 17 which is secured as by brazing to the anode 10 and tubulation 11 and to the protective cap 13 by the solder 15.

The cathode comprises a cathode disc 20 having an electron emissive coating, as of barium oxide, thereon, the disc being supported by a heater cup 21 as disclosed in Gormley et al. Patent 2,527,127. A heater 22 is positioned within the heater cup 21, the heater comprising two concentric helical coils, one lead of the heater being provided by the end of each coil away from the cathode 20. The cathode is supported by support legs 23 secured to the heater cup and held between a spring disc 24 and a bulb 27 by means of the coiled helical spring 25. The spring is supported by a spring support 26 secured to the bulb 27.

The stem of the bulb 27 comprises an expansion shield 30 of U-shaped section and having its outer end 31 secured, as by brazing, to the base of the bulb 27 and its inner end 32 forming a cup in which is positioned a stem insulator disc 33. Leads 34 extend through the disc. The leads 34 and the expansion shield 30 are secured to the insulator disc 33 by means of a glaze 35 which covers both surfaces of the disc and extends along the end 32 of the shield and between the disc and the leads 34.

The disc 33 is advantageously of F66 steatite while the leads 34 are of molybdenum and the shield 30 is of Kovar. In the fabrication of this stem the leads are fitted into their appropriate apertures in the disc 33 and the disc in the cup portion 32 of the shield 30. A few drops of a mixture of glaze with a suitable vehicle and binder are then placed on the upper surface of the disc. The glaze mixture is dried out and the stem is then glazed in a furnace. On heating, the Kovar shield having a higher thermal coefficient of expansion than the F66 steatite disc expands slightly away from the disc so that the glaze can run down between the two. Similarly, the molybdenum leads having a smaller coefficient of expansion than the steatite disc do not expand sufficiently

to maintain a tight contact with the disc and the glaze thus runs down through the apertures in the disc between it and the leads 34.

Thus the glaze spreads over both surfaces of the disc and between the disc and the metal parts. On cooling, the metal parts press against the disc compressing the interposed glaze which remains plastic over a wide range of temperatures. By this method very tight seals are realized. Advantageously, nickel may be sintered onto the Kovar shield 33 to provide better adherence for the glaze.

The remaining portions of the envelope of the tube comprise a cathode insulator 40 positioned between the upper end of the bulb 27 and a cathode platform 41 and a similar anode insulator 42 positioned between the anode connector ring 17 and an anode platform 43. An electrode frame 44 to which is attached a control grid 45 is positioned between the two platforms 41 and 43. A grid spacer ring 46 determines the cathode to grid spacing. The two platforms 41 and 43 may advantageously be joined by being welded together by means of an interposed steel welding ring 47. The grid may advantageously be of the type disclosed in our Patent 2,678,486, issued May 18, 1954.

The advantages of employing ceramic envelopes in electron discharge devices, as just described, rather than glass, have been known. Particularly by using ceramic parts in the envelope, as well as by employing a stem as described above, glass to metal seals are obviated. The avoidance of such seals removes the necessity of oxidizing any metal parts, which is a requisite step in glass to metal sealing operations. Oxidized parts present difficult problems of cleansing and to some extent they prevent a perfect cleansing of the finished tube. Further in baking the tube glass in the envelope imposes a much lower limit, such as 450° C., than ceramic which allows the tube during the baking to be heated much higher, even up to 800° C. This ability of the envelope to withstand heat allows the anode to be heated to a high temperature to remove from the honeycomb any condensed vapors that may have been deposited there which could subsequently contaminate the cathode. Additionally, the problems of cooling the anode are greatly simplified.

Prior metal to ceramic seals have been of the type in which the difference in expansivities of the materials could be employed to insure a tight seal. Thus the seals have been between rings of ceramic and metal in which the one material, on cooling, could contract around the other. The interaction of the Kovar shield 30, the steatite disc insulator 33 and the leads 34 of the stem is illustrative of these types of seals. However, for such applications as the microwave triode depicted at Fig. 1, or in minute traveling wave tubes, it is highly desirable to attain the advantages of a glassless or ceramic envelope without ring-type seals.

In order to achieve a butt seal between steatite and Kovar the following steps must be taken in accordance with our invention. Each of these steps is of prime importance and the criticalness of the limitations, with the reasons therefor, are discussed below. Considering the seal between the anode insulator 42 and the anode connector ring 17, the insulator 42 is first sprayed with a metallizing suspension of molybdenum and iron, the suspension consisting of iron and molybdenum in the proportion of 1 to 50. The iron powder can be derived from the decomposition of iron carbonyl and should advantageously be of very high purity, having a total sulphur content of less than 0.0002 per cent, carbon content of less than 0.03 per cent and only minute traces of other elements. The stringent requirement of a low sulphur content is imposed mainly to protect the cathode from possible contamination by the sulphur. The molybdenum powder should also be of the highest grade commercially obtainable, having a total sulphur content of less than 0.01 per cent. The average particle size of

these powders should be between 5 and 8 microns, in terms of Fischer sub-sieve sizer measurements. The powders may be suspended in an alcohol to separate out the larger size particles and then dried.

The powders are mixed together in a suitable suspension for spraying onto the insulators. One such suspension advantageously comprises 0.8 gram of iron fines or particles, 40.0 grams of molybdenum fines, and 10.0 grams of amyl acetate solution of nitrocellulose in 150 milliliters of a lacquer thinner. One suitable lacquer thinner consists of a mixture of solvents and aromatic diluents for nitrocellulose lacquers having the following composition:

Material:	Per cent by volume
Aromatic naphtha	60-66
Ethyl or butyl alcohol	6-0
Ethyl acetate, 85-88 per cent grade	18
Normal butyl acetate, 83-92 per cent grade	16

However, other suspensions may be employed.

While both sides of the insulator 42 are sprayed, preferably one at a time, so that the insulator may be sealed to the anode platform 43 as well as to the anode connector ring 17, the method will only be discussed with reference to the upper seal. It is important that the metallizing coating sprayed onto the insulator be smooth and even. Thus the suspension must be of entirely even consistency and homogeneity. We have therefore found it desirable to agitate the suspension for one hour before using it. Also in order to attain a completely even coating the suspension must be sprayed onto the insulator as painting it on results in an uneven coating. We have found a DeVilbiss type AG 505 spray gun with a No. 284 cap, "H" tip, satisfactory when employed with apparatus for positioning and rotating the insulator. Preferably a plurality of insulators are positioned on the periphery of a revolving turntable, the insulators themselves not rotating. Then as each insulator passes under the spray gun, a portion of the coating is sprayed onto it. The rate of rotation of the table should advantageously be such that this portion of the coating will have dried before the insulator again passes beneath the gun. We have found that this alternate spraying and drying procedure results in a more even coating than merely spraying the whole coating on at once. Also it is advantageous to agitate the contents of the spray gun cup, as by a small propeller, during the spraying operation itself to guarantee absolute homogeneity in the solution.

The insulator is sprayed to deposit a thickness of from 0.0006 to 0.0008 inch, and this thickness must be measured, as by an Ames dial gauge, to ascertain if there are any portions of the coating either above or below this range of thicknesses. If there are, these insulators are discarded. This extreme accuracy in both the smoothness of the coating and its thickness is important, and for the particular granular size particles employed these limits cannot be varied by any substantial amount. The reasons for this strict limitation on the coating thickness are given below.

The insulators are then fired in an atmosphere of wet forming gas, 72 per cent nitrogen and 23 per cent hydrogen, for twenty minutes at a temperature of from 10 to 15° C. below the initial maturing temperature of the steatite. In the fabrication of specific tubes, as shown in Fig. 1, the F66 steatite has been consistently matured at about 1260° C. so that the required firing temperature is from 1245 to 1250° C. This temperature range is critical and variations of even less than ten degrees may prove fatal. The amount of heat absorbed by the ceramic should be just enough to soften the skin or surface, as explained below. We have found that a heating duration of about twenty minutes is sufficient to thus soften the ceramic surface without overheating.

The heating of the ceramic insulator at this temperature softens the skin of the ceramic and the particles of

molybdenum and iron become embedded in the skin. If too thick a deposit of these particles has been initially coated on the insulator, there will be a top layer which is not rigidly secured to the ceramic. It would be this top layer to which the seal would be made and the connection between it and the embedded particles would not be strong enough to maintain a vacuum seal. If not enough iron and molybdenum particles are coated onto the ceramic, the entire surface will not be covered and a proper bed for the seal will not be present.

As the thickness of the coating is thus dependent on the number of particles required to just cover the surface of the insulator it is apparent that the particle size and thus the density of the coating will also determine the exact thickness of this coating. Thus where relatively large surface areas are involved somewhat larger particle sizes can be employed.

In this firing operation the forming gas is bubbled through distilled water so that it becomes "wet," i. e., has a very slight content of oxygen. By thus firing the coating on the steatite insulator at near the maturing temperature of the ceramic in an atmosphere having a very slight partial pressure of oxygen there is a controlled selective oxidation of the iron and molybdenum and the metallic oxides thus formed bond to the ceramic by fluxing with the glassy phase of the steatite. The temperature of this firing must, however, be controlled within the limits of from 10 to 15 degrees below the maturing temperature of the steatite. A lower temperature will not sufficiently soften the surface of the ceramic to allow this physical embedding of the particles whereby the oxide bond referred to above is formed. However, a temperature closer to the maturing temperature of the steatite will cause the ceramic to erupt and will thus change its chemical structure, destroying the desired properties of the material. F66 steatite is a crystalline material bonded by a glass matrix and the melting point of the matrix is fairly sharp. If the initial maturing temperature is exceeded the glass matrix melts and more crystalline material is dissolved into it. Also there is gas formed inside the insulator during its fabrication and reheating close to the maturing temperatures causes the gas to expand. The impervious skin that is over the ceramic surface first becomes roughened as the trapped gases expand and blebs or small bubbles are formed on the surface of the insulator. Upon further heating these bubbles expand and break, erupting through the skin of the surface and giving it a frothy appearance. This frothy appearance can also be caused by the reactions between the oxides in the ceramic surface and the oxides present or formed in the metallized coating, which reactions occur when the insulator is overfired. When the coating has been overfired the surface of the coating itself will appear roughened, chipped, or cracked in addition to the manifestations of the overfiring also apparent on the uncoated portions of the ceramic because of these small bubbles appearing on the smooth surface. If the coating is underfired, this condition may also be readily detected by inspection as the particles do not adhere to the insulator. These and other visual inspections referred to herein are advantageously made with a thirty power microscope.

It is also important to the protection of the desired properties of the F66 steatite that the insulator be brought to the maximum temperature at a rate of less than 50° C. per minute and that it also be brought back down to room temperature at that rate. More rapid rates of heating and cooling will cause the steatite to fracture as even F66 has a relatively poor resistance to thermal shock. Each heating of the steatite insulator therefore has imposed on it this requirement. It is particularly necessary that careful control and check be kept on the rates of heating and cooling as there are no apparent indications when serious strains have been introduced into a steatite insulator without actually fracturing it. In

the heating of glass, strains can be observed under polarized light, but steatite is not transparent. Thus failure to maintain careful control over the rates of temperature change will give rise to inexplicable failures of the steatite envelopes or seals.

A second metallizing suspension is sprayed onto the metallized ceramic surface as the molybdenum-iron surface is difficult to wet with molten solders. This second suspension comprises carbonyl nickel particles of very high purity and advantageously having a sulphur content of less than 0.005 per cent in suitable suspension. The particle size is preferably less than four microns. To prepare the nickel suspension 40.0 grams of nickel powder may be added with 10.0 grams of amyl acetate solution of nitrocellulose to 150 milliliters of the lacquer thinner described above.

The same care must be taken to insure an even coating of nickel on the insulator, the coating also preferably being of a thickness of from .0006 inch to .0008 inch. However, it is only important that sufficient nickel be coated onto the ceramic to cover the prior metallized coating and thus provide a satisfactory brazing surface. .0006 inch is apparently the minimum amount as below that there is not adequate coverage of the undercoating. While more than .0008 inch may be employed in this method, in the particular tube depicted in Fig. 1 the spacing from the anode to the cathode was required to be maintained within the range of from .010 to .012 inch so that for spacing purposes a very thin layer is specified.

In order to attain a very even coating, the nickel suspension is also advantageously agitated for an hour before use, and agitation continued during the spraying by means of a propeller rotating in the sprayer cup. After the suspension has been sprayed on, the insulator is fired in an atmosphere of wet hydrogen at a temperature and for a time sufficient to sinter the nickel to the molybdenum-iron coating. As the temperature will be considerably below the maturing temperature of the ceramic and the steatite is not affected by this operation the particular time and temperature of this firing are not critical. We have found a firing at 1100° C. for fifteen minutes to be advantageous. The hydrogen is bubbled through distilled water to attain a partial pressure of oxygen because it has been found that heating F66 steatite in a pure hydrogen atmosphere causes a reduction of some of the component oxides in the surfaces of the insulator. This slight partial pressure of oxygen prevents any determinental effects occurring to the ceramic but may be ignored in so far as the metallized coatings are concerned. The molybdenum and iron oxides on the surface of the insulator are reduced in this atmosphere because of the great excess of hydrogen and to some extent the nickel alloys with the molybdenum at the surface layer between the two coatings. Care must again be taken that the rate of heating or cooling does not exceed 50° C. per minute.

The insulator is then ready to be sealed to a Kovar part, as to the anode connector ring 17, which has been prepared by being coated with a copper surface. While the amount of copper coated onto the Kovar is not critical we have found it advantageous to employ a very small amount, advantageously approximately 10 milligrams per square inch. This thin surface aids in obtaining a good flow of silver at the time of the brazing. The copper layer however actually diffuses into the Kovar so that the coated or flashed parts quickly lose their copper color. If too much copper were employed, substantially in excess of the amounts found advantageous, the copper of course would not fuse into the Kovar and could alloy with the silver and alter the brazing temperature of the metals. Additionally, as the whole Kovar member is flashed at one time rather than only the portion to which the seal is made, the seal between the stem shield 33 and the lower end of the bulb 27 must also be considered. We have found that if the amount of copper flashed onto the Kovar is not accurately controlled the resistance of these parts

varies so that the optimum conditions for fabricating this stem seal, which is advantageously pulse brazed, will not be consistent.

The sealing between the copper flashed Kovar piece and the nickel surface of the ceramic is accomplished by positioning between them a .001 inch silver brazing washer. The amount, or volume, of silver employed is also critical to the achievement of a successful vacuum seal. When the washer is coextensive with the surface of the steatite and thus with the seal, it should be one mil, i. e., 0.001 inch, thick. Of course, thicker washers, but having the same volume of silver, could be employed. If more silver than this equivalent or actual one mil thickness is employed, the silver will have a tendency to overflow either onto the edges of the ceramic, which have not been metallized, or over onto the side of the ceramic. Then when the silver and ceramic cool strains are introduced in the ceramic resulting from shear or tension stresses, to which the ceramic is very weak. These cause cracks to appear and ultimate failure of the seal. But additionally, silver itself has certain characteristics which mitigate against any excess. Thus silver vaporizes easily and an excess of silver within the envelope of the tube would be liable to vaporize and be deposited on the various electrodes, either impairing their operation or actually short circuiting them. Also it is known that oxygen can be passed through silver by a process of forming silver oxide molecules with successive silver atoms. We have found for the tube depicted in Fig. 1 a thickness of from 0.0075 to 0.001 inch gives the minimum proper coverage. However, the width of the seal has a secondary effect on the thickness of the silver.

The brazing may be done in wet hydrogen at a temperature of 1000° C. for ten minutes, but the time and temperature will depend partially on the mass of the supporting jigs and boats and their heat capacity. It is sufficient that the temperature be raised above the brazing temperature of the silver, which is 960° C. and maintained a sufficient length of time to assure an even flow of the silver. The rate of change of temperature of course must not exceed 50° C. per minute.

The thermal coefficients of expansion of F66 steatite and of Kovar over the range of temperatures of the operation and processing of the device of Fig. 1 are shown in Fig. 2. From these curves and from the actual dimensions employed in the device of Fig. 1 the curves of Fig. 3 are prepared. In one specific embodiment of the device of Fig. 1, the mean diameter of the F66 steatite portions of the envelope, i. e., of the cathode insulator 40 and anode insulator 42, at the brazing temperature of silver, 960° C., is 0.3480 inch. As the device of Fig. 1 is shown in proper proportion an appreciation of the size of the device and its component parts and of the extreme accuracy with which the seals must be made can be gained from the size of these insulators. In fact, the over-all height of the device is only about two inches. Fig. 3 shows the variation in the mean diameter of the insulators and the variations in position of the Kovar portions adjacent the points of mean diameter at the silver brazing temperature as the temperature is reduced.

As can be seen from Fig. 3 there is a slight divergence as the materials cool from the silver brazing temperature to about 500° C. from which temperature the two curves descend almost parallel. During the operation of the device of Fig. 1, the anode seal, i. e., the seal between the anode insulator 42 and the anode connector ring 17, will attain a temperature of about 300° C. while the cathode and grid seals will attain a temperature of the order of 200° C. Thus within the range of temperatures to which the various Kovar-steatite seals are subject during the operation of the device of Fig. 1, the two curves of Fig. 3 are substantially parallel so that there is practically no tendency for the materials to alter their relative positions. The actual total shift between the two materials between 350° C. and 300° C. is only 0.19 mil. And we have

found that not only is the change of strain practically nil over the working range of the operating temperatures of the tube, but further the reheating of the seal when the tube is on the pumps and being evacuated, during which the temperature is raised to about 650° C. decreases the stresses on the seal so that no difficulty is encountered in reheating the seals.

While Fig. 3 shows the actual changes in the dimensions of the component parts of the seal, i. e., of the F66 steatite ring and the adjacent flat ends of the Kovar cylinders, it does not show the stresses involved. Thus the distance between the two curves is not indicative of the increase in stress in the seal upon cooling. This is due to another characteristic of the silver, its poor creep resistance. Little is known about this creep effect and apparently no data is available describing it as a function of temperature. Even were such data available the effects of the very thin layer of silver employed and of the interfaces between the silver, the metallized steatite, and the Kovar would probably invalidate the data for this particular application. However, we have found that this poor creep characteristic of the silver is important in the fabrication of successful steatite-Kovar seals and that as the metals being brazed do not creep, the resultant stress at the seal is far less than is implied by the distance between the two curves of Fig. 3. We have tried to make seals in which a gold alloy having approximately the same melting point as silver is employed as the brazing material but such seals were not successful due to the high stresses in the resultant seal because the gold alloy did not have a poor creep resistance.

However, by employing silver as the brazing material and carefully staying within the critical limits defined above for the various steps involved we have been able to make successful seals easily and have had no difficulty in repeating the successful fabrication of butt type seals with various batches of the materials involved.

What is claimed is:

1. The method of butt sealing a flat portion of a Kovar member to a flat surface portion of an F66 steatite member having a thermal coefficient of expansion compatible with that of Kovar which comprises spraying a suspension of molybdenum-iron particles on the flat surface portion of the steatite member to a thickness such that the particles of molybdenum and iron just cover the surface and are embedded into the surface on heating, heating the steatite member with the suspension thereon up to a temperature of from 10 to 15° C. below the maturing temperature of the steatite in an atmosphere of hydrogen, nitrogen and traces of oxygen for approximately twenty minutes, spraying a nickel suspension onto the surface of the steatite sufficient to cover the molybdenum-iron coating, sintering the nickel to the molybdenum-iron coating, copper flashing the flat portion of the Kovar member, placing a silver brazing washer between the flat portion of the Kovar member and the surface of the steatite member, and heating said members above the melting temperature of the silver and below the maturing temperature of the steatite, the maximum rate of change of temperature of the steatite member during any heating operation being 50° C. per minute.

2. The method of butt sealing a flat portion of a Kovar member to a flat surface of an F66 steatite member which comprises spraying a suspension of fine molybdenum-iron particles on the flat surface of the steatite member to a thickness such that the particles cover the surface and are embedded into the surface on heating, heating the steatite member with the suspension thereon to a temperature of from 10 to 15° C. below the maturing temperature of the steatite for approximately twenty minutes in a wet nitrogen-hydrogen atmosphere, said atmosphere being of the order of 72 per cent nitrogen and 28 per cent hydrogen with traces of oxygen, spraying a suspension of fine nickel particles onto the

metallized surface of the steatite member sufficient to cover the molybdenum-iron coating thereon, heating the steatite member with the nickel suspension thereon in a wet hydrogen atmosphere to a temperature sufficient to sinter the nickel particles to the molybdenum-iron coating, coating a thin layer of copper onto the flat portion of the Kovar member, positioning a silver brazing washer of approximately one mil thickness between the flat portion of the Kovar member and the metallized surface of the steatite member, and heating said members above the melting temperature of the silver and below the maturing temperature of the steatite, the maximum rate of change of temperature of the steatite member during any heating operation being 50° C. per minute.

3. The method of butt sealing a flat portion of a Kovar member to a flat surface of an F66 steatite member which comprises spraying onto the surface of the steatite member a suspension of 5 to 8 micron molybdenum-iron particles to a thickness of from 0.0006 to 0.0008 inch, heating the steatite member to a temperature from 10 to 15° C. below the maturing temperature of the steatite for twenty minutes in an atmosphere of approximately 72 per cent nitrogen, 28 per cent hydrogen and traces of oxygen to embed the particles into the surface of the steatite, spraying a suspension of fine nickel particles onto the metallized surface of the steatite so that a thickness of more than 0.0006 inch is deposited, heating the steatite in a wet hydrogen atmosphere to a temperature sufficient to sinter the nickel to the molybdenum-iron surface, coating a thin layer of copper onto the Kovar member, interposing between the flat portion of copper coated Kovar member and the metallized surface of the steatite member a silver brazing washer of approximately one mil thickness, and heating the Kovar member, steatite member, and interposed silver washer above the brazing temperature of the silver and below the maturing temperature of the steatite, the maximum rate of change of temperature of the steatite member during any heating operation being 50° C. per minute.

4. The method of butt sealing a flat portion of a Kovar member to a flat surface of an F66 steatite member which comprises spraying onto the surface of the steatite member a molybdenum-iron suspension having particles of from 5 to 8 microns so that a thickness of from 0.0006 to 0.0008 inch is deposited thereon, heating the steatite member with the suspension thereon up to a temperature of from 10 to 15° C. below the maturing temperature of the F66 steatite for twenty minutes in an atmosphere of wet 72 per cent nitrogen, 28 per cent hydrogen, spraying a suspension of nickel particles onto the metallized surface of the steatite, the particles being of approximately 4 microns and a thickness of more than 0.0006 inch being deposited thereon, heating the steatite with the nickel suspension thereon in a wet hydrogen atmosphere to sinter the nickel to the molybdenum-iron surface, copper flashing the Kovar member, interposing between the Kovar member and the metallized surface of the steatite member a silver washer having a volume equivalent to a thickness of one mil over the area of the seal, and heating the Kovar member, steatite member, and interposed silver washer to approximately 1000° C., the maximum rate of change of temperature of the steatite member during any heating operation being 50° C. per minute.

5. The method of butt sealing a flat portion of a Kovar member to a flat surface of an F66 steatite ring having been cured at approximately 1260° C. which comprises spraying onto the surface of the steatite member a suspension of molybdenum-iron particles in the ratio of 50 to 1 and of a size from 5 to 8 microns so that a thickness of from 0.0006 to 0.0008 inch is deposited thereon, heating the steatite member with the suspension thereon up to a temperature of from 1245 to 1250° C. for twenty minutes in an atmosphere of 72

per cent nitrogen, 28 per cent hydrogen with traces of oxygen, spraying a suspension of approximately 4 micron nickel particles onto the metallized surface of the steatite to a thickness of more than 0.0006 inch, heating the steatite with the nickel suspension thereon to a temperature of approximately 1100° C. for fifteen minutes in a wet hydrogen atmosphere, coating approximately 10 milligrams per square inch of copper onto the Kovar member, interposing between the copper flashed Kovar member and the metallized surface of the steatite ring a silver washer approximately one mil thick, and heating the Kovar member, steatite ring, and interposed silver washer to a temperature of approximately 1000° C. for ten minutes, the maximum rate of change of temperature

of the steatite ring during any heating operation being 50° C. per minute.

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