June 10, 1958 H. BENDER 2,838,390

METHOD OF MAKING METAL-TO-CERAMIC SEALS

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FIG. 1.

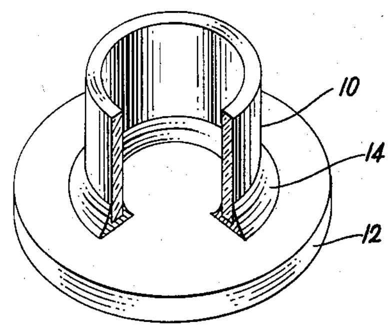
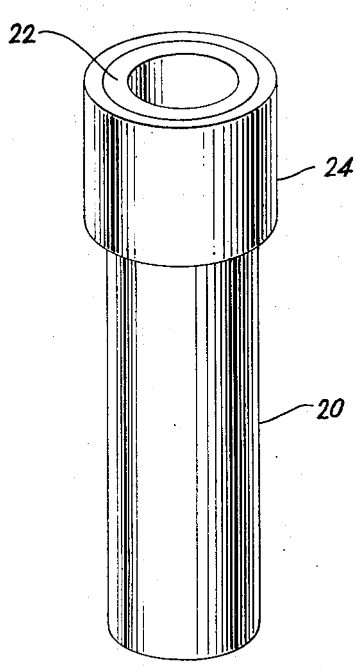


FIG. 2.



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METHOD OF MAKING METAL-TO-CERAMIC SEALS

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7 Claims. (Cl. 75—.5)

This invention relates to an alloy and an improved method of making metal-to-ceramic seals. This application is a continuation-in-part of application Serial No. 380,533, filed September 16, 1953 now U. S. Patent No. 2,805,944.

Many processes and materials have been developed for metallizing non-metallic refractory bodies, such as in making ceramic-to-metal seals. The joining of ceramic bodies to metals or ceramic bodies to each other in a gas tight manner has become more and more important, and in some cases necessary for the proper functioning of certain electronic equipment. Probably the simplest process shown in the prior art is the so-called silver-paste technique for applying metal to the ceramic body. Though satisfactory for some uses, this process does not yield a completely satisfactory gas-tight bond. When the bond formed in this manner is subjected to certain types of abrasive action, the metal put on the ceramic body has a tendency to peel off and thus destroy the gas-tight seal. Among the other methods devised, considered to give good results is the so-called Telefunken process in which molybdenum is used in promoting the metal-to-ceramic bond. When this method is used with the proper ceramics and under the right temperature conditions, excellent vacuum-tight seals can be obtained between the metal bodies and the ceramics. However, the disadvantage with this process is that it must be carried out in several steps, and further that it is limited in its application to the bonding of materials whose coefficients of expansion are matched.

It is an object of the present invention to provide an improved method for metalizing non-metallic refractory bodies, particularly for making ceramic-to-metal seals. Advantageously, the improved method can be carried out in a single step.

It is a further object to provide an alloy for making ceramic-to-metal or ceramic-to-ceramic seals which can be used successfully in the bonding together of materials which have to withstand fairly high temperatures.

It is a further object of this invention to provide a material and an improved method for bonding together of such bodies whose coefficients of expansion may vary over relatively wide range.

In accordance with the present invention it has been found that one or more of the above objects as well as other advantages can be attained by the use of lead base alloy powders containing at least 0.5% of copper and at least 0.1% of titanium in admixture therewith.

The above and still further objects, features and advantages of the present invention will be best appreciated by reference to the following detailed description, when taken in conjunction with the accompanying drawing, wherein:

Fig. 1 is a perspective view showing two ceramic bodies bonded together in accordance with features of the present invention; and,

Fig. 2 is a perspective view of a metal tube which has

been metallized at one end thereof in accordance with further features of the present invention.

The material for making the metal-ceramic seals in accordance with the present invention is a bonding mixture of an alloy powder with powdered titanium or titanium hydride or zirconium or zirconium hydride. The alloy powder is made up of lead and copper which have been melted together and cooled in such a way as to produce a powder with a uniform and intimate mixture of lead rich and copper rich phases such as are known to form in this system. The copper is present in an amount not less than 0.5%. The titanium or zirconium powder which is to be used in conjunction with the alloy powder is present in the mixture in an amount not less than 0.1%. These materials may be present either in the form of titanium or zirconium metal powders or in the form of their respective hydrides. With this powder mixture it is possible to make a good ceramic-to-metal or ceramic-to-ceramic seal bonded with a metal bond. Advantageously, this can be done in a single step operation and is not limited to the bonding together of bodies having similar coefficients of expansion. The widest latitude and variation of coefficients of expansion can be tolerated when the alloy powder has a high percentage of lead.

The bonding mixture is preferably made up by suspending the alloy powder and the zirconium or titanium metal in a binding agent, such as a lacquer. This lacquer suspension can then be applied to the ceramic at the junction where the bond is to take place by simply coating this area of the ceramic with the suspension, as by painting, dipping, or spraying. Formulation of lacquer suspension is very simple in that the alloy powder can be obtained in the commercial market at varying percentages of its two constituent materials, namely the lead and copper. The highest amount of copper which has been used successfully to date is an alloy powder in which the copper is present in the amount of 75% and the lead in the amount of 25%. This alloy powder is then simply mixed in a mechanical manner with the proportion of titanium or titanium hydride or zirconium or zirconium hydride which is desired, and then incorporated in the lacquer suspension.

The lacquer suspension of the bonding mixture can be used to form the bond or seal between ceramic parts by taking the ceramic parts which are to be bonded together and subjecting them to a simple cleaning operation to remove any foreign materials which may be on the surface. After coating the cleaned surface with the bonding suspension, a butt joint or the like may be formed by contacting the cleaned and coated surfaces. The abutted material is then heated in a non-oxidizing atmosphere.

Another technique which can be used to advantage with these alloys is to mix the powdered constituents dry and to fabricate sheet, wires, washers, or other preforms by the accepted methods of powder metallurgy. With appropriate sintering and annealing treatments, as determined by the copper:lead ratio, the material becomes ductile and can be rolled to sheet. In certain applications it may be more advantageous to use solid preforms made as just described to form the seal. In use, the bonding preform is placed at the site of the desired bond and the assembly heated in a non-oxidizing atmosphere, as described.

To obtain best results the parts can be heated to a temperature of about 700–1100° C. for a period of about three minutes. The higher temperatures are preferably used in those cases in which the copper content of the alloy powder is above 20%. The lower temperatures in the order of 700–800° C. are used in those cases in which the copper content is fairly low. After heating of the assembly at appropriate temperatures followed by cooling, it will be found that the parts are joined in a vacuum-tight manner, the interposed metal is tightly bonded to the ceramic, and said metal can not be peeled off or cut away from the ceramic material.

This process is very simple in nature. Further, the process requires no formidably technically detailed steps for the preparation of the bonding material and yet results in the formation of a very good vacuum-tight bond between the parts which have been joined. Still further, the process can be carried out in a very simple non-oxidizing furnace in which the atmosphere is either hydrogen, vacuum, or some other inert gas, such as argon or helium.

Fig. 1 of the drawings shows two ceramic parts which have been bonded together as previously described. The bonded assembly includes a tubular piece **10** of ceramic which is joined to a disc-like wafer **12** of ceramic by means of an interposed layer of mass of alloy **14** embodying feature of the present invention.

In Fig. 2 there is shown a tubular member **20** which has been coated at locations extending inwardly from one end **22** with the present alloy to form a metallized surface **24**.

The wetability of the present alloy is very good. Although the composition of the alloy can be varied considerably, it has been found that excellent results can be obtained with alloys in which the copper content ranges from 0.5 to as high as 75%. Naturally the higher the copper content of the alloy, the more temperature resistant is the seal which is produced. In those cases in which low temperature seals are preferred since mismatching of the coefficients of expansion are at their worst, alloys containing up to 7% copper have given the best results. With the present composition and method it has been found possible to bond two weak ceramics such as forsterite or steatite. The titanium content of the mixture may also vary over quite a range. It should, of course, be at least 0.1% titanium or its equivalent in the form of titanium hydride or zirconium or zirconium hydride but good results have been obtained with amounts up to 10%. Although all amounts up to 10% have been used quite successfully, it is preferred to make use of smaller amounts of titanium or zirconium or their respective hydrides, for example in the range of .1 to 3%. The Pb-Cu-Ti ternary system has shown clearly superior wetting and bonding compared to binary systems such as Cu-Ti and Pb-Ti, suggesting that a ternary reaction between the components is more effective in promoting bonding than known ternary reactions between the components.

While the above description and drawings disclose a preferred and practical embodiment of the composition and method of making a metal-to-ceramic seal of the present invention, it will be understood that the specific details shown and described are by way of illustration and are not to be construed as limiting the scope of the invention.

What I claim is:

1. A material suitable for the bonding of metal-to-ceramics or ceramics-to-ceramics consisting essentially of a powdered alloy of lead and copper in which the copper ranges from 0.5 to 75% in admixture with powdered titanium in an amount not less than 0.1%.

2. A material suitable for the bonding of metal-to-ceramics or ceramics-to-ceramics consisting essentially of a powdered alloy of lead and copper in which the copper ranges from 0.5 to 75% in admixture with powdered zirconium in an amount not less than 0.1%.

3. A material suitable for the bonding of metal-to-ceramics or ceramics-to-ceramics consisting essentially of a powdered alloy of lead and copper in which the copper ranges from 0.5 to 75% in admixture with a powdered metal of the group of zirconium and titanium in an amount not less than 0.1% of said powdered metal.

4. A material suitable for the bonding of metal-to-ceramics or ceramics-to-ceramics consisting essentially of a powdered alloy of lead and copper in which the percentage of copper lies within the range of 0.5 to 75% in admixture with a powdered metal of the group of titanium and zirconium in which the powdered metal lies within the range of 0.1 to 10%.

5. A material suitable for the bonding of metal-to-ceramics or ceramics-to-ceramics consisting essentially of a powdered alloy of lead and copper in which the copper ranges from 0.5 to 75% in admixture with a powdered metal selected from the group of titanium and zirconium and their respective hydrides in which the powdered metal lies within the range of 0.1% to 10%.

6. A material suitable for the bonding of metals-to-ceramics or ceramics-to-ceramics consisting essentially of a powdered alloy of lead and copper in which the percentage of copper lies within the range of 0.5 to 75% in admixture with a powdered metal of the group of titanium and zirconium in which the powdered metal lies within the range of 0.1 to 3%.

7. A material suitable for the bonding of metals-to-ceramics or ceramics-to-ceramics consisting essentially of a powdered alloy of lead and copper in which the percentages of copper lies within the range of 0.5 to 75% in admixture with a powdered metal selected from the group of titanium and zirconium and their respective hydrides in which the powdered metal lies within the range of 0.1 to 3%.

References Cited in the file of this patent

UNITED STATES PATENTS

935,863	Rossi	Oct. 5, 1909
1,228,017	Gleason	May 29, 1917
2,220,961	Kern	Nov. 12, 1940
2,366,954	Brooks	Jan. 9, 1945
2,386,628	Nazzewski	Oct. 9, 1945
2,466,700	Grodsky	Apr. 12, 1949
2,496,346	Haayman et al.	Feb. 7, 1950

FOREIGN PATENTS

645,003	Great Britain	Oct. 25, 1950