United States Patent

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[54] **CERAMIC TO METAL SEAL**
8 Claims, No Drawings

[52] **U.S. Cl.** **29/473.1,** 29/195, 29/504
[51] **Int. Cl.** **B23k 31/02**
[50] **Field of Search** 29/473.1, 472.7, 504, 195

[56] **References Cited**

UNITED STATES PATENTS

2,857,663	10/1958	Beggs	29/473.1
2,859,512	11/1958	Dijksterhuis et al.	29/473.1
3,091,028	5/1963	Westbrook et al.	29/473.1
3,395,993	8/1968	Bristow	29/473.1 X

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ABSTRACT: This disclosure is directed to metal to refractory seals wherein a ductile 50 atomic percent alloy of a group IV*b* metal with a group VIII metal of the same period is used to braze ceramic to metal. A preferred example is sealing Tantalum or Niobium to alumina with a 50 *a/o* Ti-Ni alloy braze.

CERAMIC TO METAL SEAL

The present invention relates to the bonding of nonmetallic refractory members to metal members, and more particularly to a temperature resistant, oxidation resistant metal to ceramic seal capable of use in cesium environments.

The problems involved in obtaining satisfactory ceramic to metal seals are well known, and various brazing alloys have been suggested by workers in the art, as in, for example, U.S. Pats. Nos. 3,091,028 and 2,857,663. Such seals are important to satisfactory operation of high power electron tube devices and are notably so in devices employing metal vapors or liquid therein such as arc devices and thermionic converters.

A common prior art method of making such seals involves first placing a layer of metal on the surface of the ceramic body or member then brazing the metal body or member to the metallized ceramic with the aid of a fusible metallic shim therebetween. Any of the several diverse metal to metal interfaces present in the so sealed structure may have a brittle intermetallic phase in the metal junction due to interaction between metal, braze, and metallized ceramic. Besides the high failure rate, the joint or seal as a whole may be weak due to the various intermetallic phases present. Eliminating the metallizing step and brazing directly to the ceramic body offers promise for more facile sealing techniques, even better seals. The braze metal must then be some material which reacts strongly with the ceramic in order to achieve the desired bond. Yet, the high chemical reactivity of such a braze metal may cause the braze also to react strongly with the metal member. Thus, if a pure metal braze is employed, the solution resulting from dissolution of the metal body and the braze metal has a progressively lower melting point than the pure braze metal and substantial, even complete, dissolution of the metal body can result if the completed seal is subjected to high operating temperatures. On the other hand, if a eutectic braze is employed, the metal from the metal body which dissolves therein often forms a brittle intermetallic phase between itself and one or both of the braze constituents.

In any event, an upper operating limit of about 500° C. is commonly set for the ultimate equipment sealed by conventional brazing alloys and the heretofore employed ceramic to metal sealing techniques.

An object of the present invention is to provide an improved bond for joining nonmetallic refractory bodies to metallic members.

A further object of the invention is to provide a ceramic to metal seal having good compatibility with a cesium environment and operation at elevated temperatures.

Still another object of the invention is to provide a high quality ceramic to metal seal employing a ductile metal braze.

Further objects and the advantages of the present invention will be apparent from the description thereof which follows.

Briefly stated, the practice of the present invention comprises forming the seal with a 50 atomic percent alloy of one member selected from the group IVb metals and the other member selected from the group VIII metals of the same period. More specifically, the alloys contemplated for the braze material are the 50 *a/o* alloys of: titanium with iron, cobalt, nickel or mixtures thereof; hafnium with osmium, iridium, platinum, or mixtures thereof; zirconium with rhodium, ruthenium, palladium, or mixtures thereof.

Most significant in terms of the ceramic to metal seal is that this group of 50 atomic percent alloys or intermetallic compounds are ductile and have a significant homogeneity range on either side of the 50 *a/o*. They remain ductile within this range of homogeneity. Thus, the Ti-Ni system has a homogeneity range of 46—53 *a/o* Ti. The other systems have similar, but not necessarily identical homogeneity ranges. For further description of the alloys per se reference is made to a series of articles by F. E. Wang or F. E. Wang et al. in Journal of Applied Physics, Vol. 36, p. 3232 (1965); Vol. 38, p. 822 (1967); and Vol. 29, p. 2192 (1968). Attention is directed also to U.S. Pat. No. 3,174,851 for description of the 50 *a/o* Ti-Ni alloy.

While reference has been made above to 50 *a/o*, the ductile alloy brazes contemplated for practice of this invention may be of any specific composition within their homogeneity range. Therefore, within the context of this invention a general reference to these alloy brazes as 50 *a/o* ductile alloys should be taken as a reference to include the entire range of homogeneity. As a practical matter the braze alloy composition should be held within somewhat narrower limits than the entire homogeneity range, 50 *a/o*±2 *a/o* being preferred.

When the IV*b*—VIII ductile 50 *a/o* alloys are used as brazes to join ceramic bodies to metal members, they perform in a beneficial and perhaps unique manner. The molten alloy reacts with the ceramic to form a hermetic joint, eliminating need for preliminary metallizing of the ceramic. Moreover, the braze reacts only slightly with the metal member in the seal assembly. Any intermetallic reaction products between the braze alloy and the metal member are not precipitated as a brittle intermetallic phase. After the seal has been formed no subsequent conditioning steps are needed. These ductile 50 *a/o* alloy brazes have general applicability to the many refractory ceramics usually joined to metal members, including for example, alumina, zirconia, magnesia yttria, sapphire. They have, also, general applicability to the metals usually joined to ceramics for electronic uses, including for example, tantalum, niobium, the group VIII metals. Importantly, they can be used at elevated temperatures, e.g. to 800° C.

One exemplary instance of a preferred embodiment of practice according to the invention is formation of a seal between a niobium member or a tantalum member and a high purity alumina body with a ductile 50 *a/o* alloy of titanium-nickel.

Use of these ductile 50 *a/o* alloy brazes permits seal fabrication by relatively uncomplicated techniques. According to one method, the ceramic body and the metal member to be joined are juxtaposed with a shim or wire of the chosen intermetallic alloy placed between them. This assembly is then heated, e.g. in a vacuum furnace or by radio frequency induction heating in an argon atmosphere to the melting point of the chosen alloy, at which point the molten alloy reacts with and wets the ceramic body and also brazes to the metal member. The braze material remains as a single phase ductile intermetallic alloy. Thereafter the assembly is cooled as rapidly as the ceramic will allow. The joint is ready for use without further conditioning. It is airtight, heat and oxidation resistant and stable for use over extended periods of time; it may be employed in a cesium environment,

For further understanding of the invention more detailed specific examples of the practice thereof is now presented.

A nickel titanium alloy of exactly 50 *a/o* employed as the braze alloy had the following properties:

Density	6.45 g./cc.
Melting point	1250° C.
Electrical resistivity (room temperature)	80 μΩcm.
Expansion coefficient	10.4×10^{16} ° C.^{11}
Ultimate tensile strength	140,000 p.s.i.
Yield strength	81,000 p.s.i.
Young's Modulus	11×10^{6} p.s.i.
Tensile elongation	up to 15 percent

A washer (0.005 inches thick) of the alloy was placed at the bottom of a tantalum cup and a high purity alumina tube was placed on top the washer. The so assembled cup, washer and tube was heated inductively in a stream of commercial grade argon to a temperature just above 1250° C. to melt the washer. The assembly was then cooled in the argon stream and removed, with the whole heating, melting and cooling process taking about 5 minutes. Examination of the cooled assembly showed that very little dissolution of the tantalum had taken place during the brief period the braze was molten and that an airtight satisfactory seal was formed.

In the same fashion a 50 *a/o* hafnium-iridium braze alloy washer formed a good seal between a tantalum cup and an alumina tube.

Sealed assemblies, sealed by the 50 *a/o* Ti-Ni, braze alloy in the manner described above were fully fabricated and tested for temperature resistance in the presence of cesium. They proved satisfactory at elevated temperatures up to 800° C.

In the same fashion a tantalum tube was brazed to magnesia with the above 50 *a/o* Ti-Ni alloy. In this instance the differential expansion between magnesia and tantalum caused the magnesia to crack upon cooling, but the seal itself appears satisfactory.

What we claim is:

1. A metal to ceramic seal which consists essentially of a ductile brazing alloy interposed between the metal and ceramic, said alloy consisting essentially of a single phase ductile alloy within the range of 48 *a/o*—52 *a/o* of titanium with a member selected from the group consisting of Fe, and Co and mixtures thereof.

2. A seal as in claim **1** wherein said ceramic is alumina, said metal is selected from the group consisting of Tantalum and Niobium and said 50 *a/o* brazing alloy is a Ti-Fe or Ti-Co alloy having a composition range of 50 *a/o*± 2 *a/o*.

3. A metal to ceramic seal which consists essentially of a ductile brazing alloy interposed between the metal and ceramic, said alloy consisting essentially of a single phase ductile alloy within the range of 48 *a/o*—52 *a/o* of zirconium with a member selected from the group consisting of Ru, Rh and Pd and mixtures thereof.

4. A metal to ceramic seal which consists essentially of a ductile brazing alloy interposed between the metal and ceramic, said alloy consisting essentially of a single phase ductile alloy within the range of 48 *a/o*—52 *a/o* of hafnium with a member selected from the group consisting of Os, Ir, Pt and mixtures thereof.

5. A method of bonding a metal member and a nonmetallic refractory body which consists essentially of interposing therebetween a preform of a single phase ductile alloy within the range of 48 *a/o*—52 *a/o* of titanium with a member selected from the group consisting of Fe and Co, and mixtures thereof, then melting only said alloy under nonoxidizing conditions, and thereafter cooling the assembly whereby said alloy forms a tight high temperature resistant bond between the metal member and the refractory body.

6. The method of claim **5** wherein said ceramic is alumina, said metal is selected from the group consisting of Tantalum and Niobium and said 50 *a/o* brazing alloy is a Ti-Fe or Ti-Co alloy having a composition range of 50 *a/o*± 2 *a/o*.

7. A method of bonding metal member and a nonmetallic refractory body which consists essentially of interposing therebetween a preform of a single phase ductile alloy within the range of 48 *a/o*—52 *a/o* of zirconium with a member selected from the group consisting of Ru, Rh, Pd and mixtures thereof, then melting only said alloy under nonoxidizing conditions, and thereafter cooling the assembly whereby said alloy forms a tight high temperature resistant bond between the metal member and refractory body.

8. A method of bonding a metal member and a nonmetallic refractory body which consists essentially of interposing therebetween a preform of a single phase ductile alloy within the range of 48 *a/o*—52 *a/o* of hafnium with a member selected from the group consisting of Os, Ir, Pt and mixtures thereof, then melting only said alloy under nonoxidizing conditions, and thereafter cooling the assembly whereby said alloy forms a tight high temperature resistant bond between the metal member and the refractory body.

PO-1050 (5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

atent No. 3,594,895 Dated July 27, 1971

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 58, for "$10.4x10^{16}$ $^{o}C^{11}$" read--- 10.4^{-6} $^{o}C^{-1}$---; and Column 3, line 1 through line 3 should read---In the same fashion a 50 a/o zirconium-palladium braze alloy washer and a 50 a/o hafnium-iridium braze alloy washer formed a good seal between a tantalum cup and an alumina tube.---.

Signed and sealed this 12th day of September 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents