Jan. 11, 1955 D. M. WROUGHTON ET AL 2,699,015

METAL MIXTURE FOR SEALING TO GLASS

Filed Feb. 27, 1951

Fig. 3.

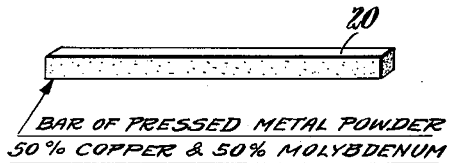


Fig. 5.

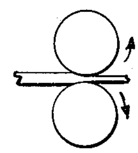


Fig. 7.

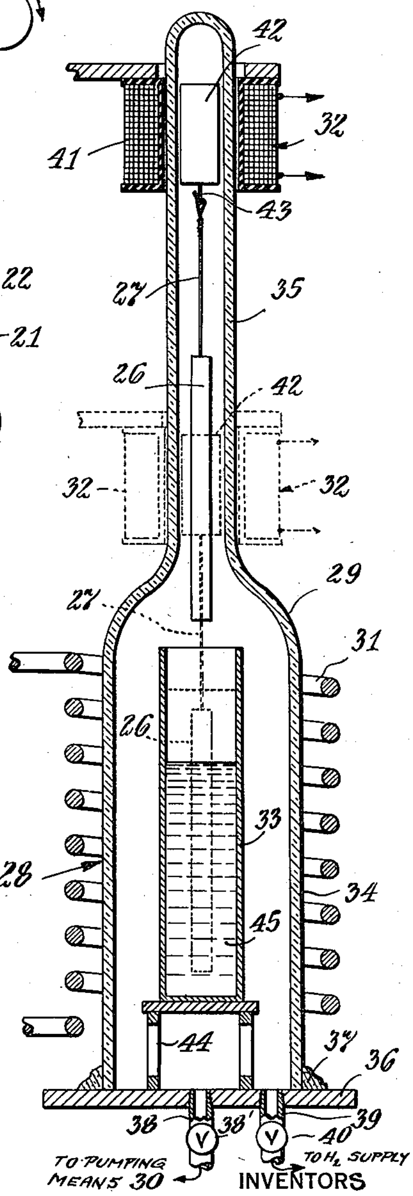


Fig. 4.

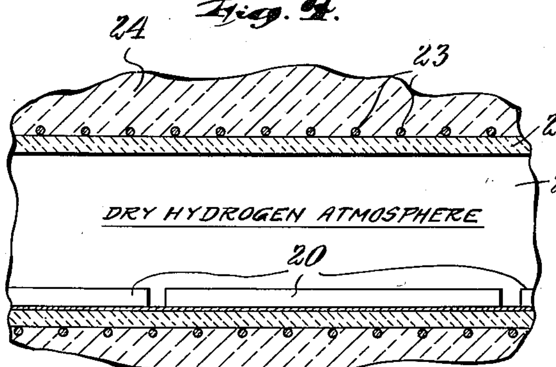


Fig. 1.

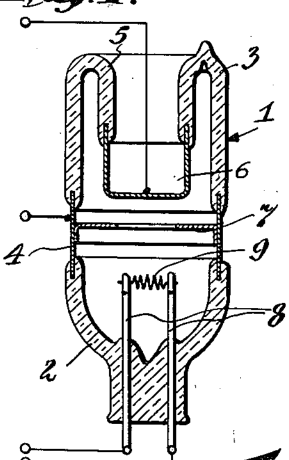


Fig. 2.

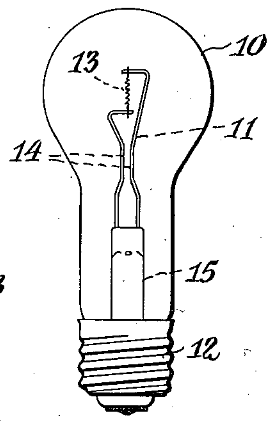
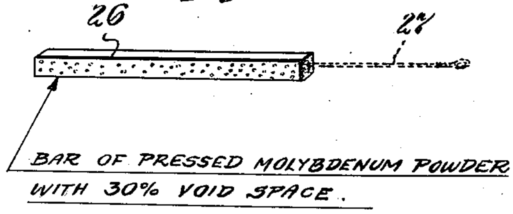


Fig. 6.



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METAL MIXTURE FOR SEALING TO GLASS

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2 Claims. (Cl. 49—92.5)

This invention relates to metal-glass seals and more particularly to metal mixtures for sealing to glass.

In sealing a wire or article of metal into glass, the principal problem involved is finding a metal with a coefficient of thermal expansion approximating that of the glass. In vacuum-tight metal-glass seals, articles of the pure metals, tungsten, molybdenum, zirconium, titanium, platinum and copper may be sealed into the proper glass having a coefficient of thermal expansion nearly the same as that of the metal in each selected instance. If the metal part to be sealed into the glass is copper and has a very thin edge in contact with the glass, all glasses may be used. Otherwise, for use with soft glass, only platinum and titanium of this pure metal group are practical.

Further, for example, in the case of stem making for electric lamps and electronic tubes, another desirable property of the metal lead-in conductor which is intended to carry an electrical current through the glass press of the stem, is that the lead should have a low specific resistance.

In the stem-making case, composite lead-in conductors, such as copper-clad steel, can be matched in thermal expansion with an appropriate soft glass, but because of their small total cross section, their resistivity is high. Further, alloys of selected metals with proper expansion coefficients can be employed, but again, the specific resistance would doubtlessly be characteristically above desired limits.

In low priced lamp and electronic tube glass stem manufacture, wherein a metallic leading-in conductor is passed through a soft glass press of a stem, it is often necessary to select a given soft glass for said stem to avoid an expensive and large graded seal between the glass envelope of the lamp or tube and the stem. Here the problem may be that of arriving at a metal having a coefficient of thermal expansion approximating that of the glass. In some soft glass instances, the available matching metals, as for example, platinum and titanium, are limited in number and extremely expensive.

Hence, it has been found advantageous, according to our invention, to provide a simple mixture of two metals, such as copper and molybdenum, which will not alloy appreciably, and which have the proper thermal expansion for matching a given glass. By mixing powdered copper and molybdenum in desired quantities, pressing, and sintering, or by infusing molten copper into the interstitial spaces of a molybdenum bar of predetermined porosity, a mixture of the pure metals can be obtained having a desired resulting coefficient of thermal expansion. Said coefficient is determined by the proportionate volumes of the pure copper and pure molybdenum in the mixture. The copper will wet and adhere to molybdenum very well, but will not alloy with the molybdenum appreciably. Thus the mixture of two pure metals has the excellent conductivity of two good conductors and a desirable resulting low specific resistance.

Further, metals such as copper and molybdenum are diamagnetic and in high frequency devices would reduce radio frequency internal losses. The presence of the pure molybdenum in the mixture produces good strength, while the pure copper in the mixture lends some ductility for bending in the cold state.

In its general aspect, the present invention has the objective of overcoming the aforementioned disadvantages of the prior art soft glass stem making and metal-glass seals.

Specifically, an object of the present invention is a

lead-in conductor or metal part for sealing into soft glass, comprising a mixture of two non-alloying metals which will match the coefficient of expansion of most soft glasses.

Another and specific object of the present invention is a lead-in conductor or metal part for sealing into soft glass, comprising a mixture of two non-alloying metals which will have a high electrical conductivity.

A further object of the present invention is a lead-in conductor or metal part for sealing into glass, comprising a mixture of two non-alloying metals which is diamagnetic and has resulting low losses in high frequency devices.

An additional object of the present invention is a lead-in conductor or metal part for sealing into soft glass, comprising a mixture of two non-alloying metals which is strong and stiff.

A still further object of the present invention is a lead-in conductor or metal part for sealing into soft glass, comprising a mixture of two non-alloying metals which is sufficiently ductile for shaping and bending.

Other objects of the invention will appear to those skilled in the art to which it appertains as the description thereof proceeds, both by direct recitation thereof and by implication from the context.

Referring to the accompanying drawing, in which like numerals of reference indicate similar parts throughout the several views:

Fig. 1 is a section of a gas filled thyratron device embodying our invention;

Fig. 2 is a perspective view of a street series type incandescent lamp;

Fig. 3 is a perspective view of a bar of a pressed powdered metal mixture of copper and molybdenum;

Fig. 4 is a longitudinal sectional view of a hydrogen furnace for sintering the bar of Fig. 3;

Fig. 5 is an end view of apparatus which may be used for rolling the sintered bar after removal from the furnace of Fig. 4;

Fig. 6 is a perspective view of a porous bar of pressed molybdenum powder; and

Fig. 7 is a section of an impregnating apparatus for infusing copper into the void space of the molybdenum bar of Fig. 6.

Referring to the electric translation device or gas-filled thyratron of Fig. 1, a closed envelope **1** is provided which comprises a basal cup-like portion **2**, a head portion **3** thereabove, both preferably soft glass and an intervening neck or metallic grid cylinder **4**, wherein our invention is included and which is sealed at its end peripheral margins to the basal and head portions respectively. Thyratron is the trade name for an electronic tube in which the unidirectional flow of electron current through an inert gas may be started by impressing an electrostatic charge on the control electrode. While a gas-filled thyratron has been arbitrarily selected for illustrative purposes, the invention is not to be understood as restricted to employment with thyratrons only.

Said head portion **3** is preferably reentrant, as at **5**, its upper part, so as to provide a downwardly directed margin within the outer wall of the head. From this reentrant portion **5** depends a cup-shaped anode **6** wherein also our invention is included. The said downwardly directed margin of the reentrant part of the head is sealed to the upper edge margin of the cup **6** peripherally thereof.

Inside grid cylinder **4** is a metallic cup-like grid partition **7** which is joined, as by welding, along the periphery of its flanged edge to the inner surface of cylinder **4**. Said partition **7** has a suitable axial center hole to permit electron passage therethrough.

Projecting through and sealed to basal portion **2** in spaced axial alignment are two parallel lead-in conductors **8** wherein also our invention is embodied. Appropriately mounted on the internal extremities of these conductors **8** is a thoriated tungsten filament or cathode **9**.

After sealing, this thyratron is given the usual exhaust which may comprise baking, induction treating, cathode sintering, final fill with gas such as xenon and tip off.

The street series type incandescent lamps, as shown in Fig. 2, comprises a soft glass envelope **10**, a filament mount **11**, sealed to said envelope, and a base **12**. While a street series type incandescent lamp has been arbitrarily selected for illustrative purposes, the invention is not to be understood as restricted to employment with only such lamps. Said mount **11** consists of a high current, low voltage, filament **13** mounted axially on lead-in conductors **14**, involving our invention, of a soft glass stem **15**.

In accordance with the usual practice, the lamp is sealed, exhausted and based. During exhaust, the lamp may be baked, flushed and pumped, and given a final fill of a gas such as nitrogen.

The method of making parts for sealing to soft glass, such as grid cylinder **4** and cup-shaped anode **6** of Fig. 1, and lead-in conductors such as conductor **8** of Fig. 1, or conductors **14** of Fig. 2, for sealing through soft glass, wherein our invention is contained, is shown in Fig. 3 through Fig. 7 of the accompanying drawing.

According to our invention, in Fig. 3, the reference numeral **20** designates a bar of a mixture of, for example, 50% molybdenum and 50% copper by volume. Said bar **20**, as shown in Fig. 3, may be made by mixing fine powders of the molybdenum and copper having particles capable of passage through a 200 mesh/inch screen.

The mixture is then pressed at high pressure in a steel mold into a bar having a cross-section, suitably ¼″ square. The pressed bar **20** is sintered for two hours at 1050° C. in a dry hydrogen atmosphere of a furnace **21**, such as is shown in Fig. 4.

Said furnace **21** may consist of a refractory tube **22** with movable doors (not shown) at each end, a resistance heating element **23** coiled about said tube, powdered insulating material **24** such as magnesium oxide, packed about said coil and tube, and a fire brick enclosing structure (not shown). The sintered bars are then rolled between high pressure rolling means or the like, as shown in Fig. 5, to form a lead-in conductor such as conductor **8** of Fig. 1 or conductors **14** of Fig. 2 of the desired circular cross-section. The rolling operation eliminates any voids or minute spacings in the mixture and produces a density of 99% to 100% of theoretical density as calculated from volume percentages.

Further, according to our invention, a lead-in conductor, such as conductor **8** of Fig. 1, may be produced by an alternative infusion or impregnation method as shown in Figs. 6 and 7. A pulverized mass of pure molybdenum powder is pressed in a suitable steel mold into a porous bar **26** of approximate ¼″ square cross-section at a pressure such that a desired void space, for example, 30% exists in the pressed bar. This interstitial void space corresponds to the desired copper composition by volume of bar **26** after impregnation. Affixed, as by welding, to one end of bar **26** are suitable suspension or mounting means, in this case a refractory wire **27** having a loop at its unattached extremity. Molten copper is then infused into the porous molybdenum bar **26** by means of the impregnating apparatus **28** of Fig. 7.

Said impregnating apparatus **28** comprises essentially a "Vycor" or quartz induction bottle **29**, pumping means **30** (not shown) an induction heating coil **31**, elevating means **32** for the work, and an open-ended refractory metal container **33**.

Open-ended circular "Vycor" bottle **29** may consist of a lower induction heating portion **34** near the open end, conforming in configuration to the usual induction bottle of this type, and an upper closed end portion **35** axial with lower portion **34** and having a smaller cross-section than said lower portion. Said bottle **29** is supported on a metallic mounting plate **36** and sealed thereto near the open end of the bottle by suitable vacuum sealing means **37**, such as silicone putty. Through a convenient hole in plate **36**, connection is made to valve **38′** and pumping means **30** by an exhaust pipe **38**, handily joined to the plate **36** as by brazing. Also depending below plate **36** and affixed thereto along the side walls of an appropriate hole in a vacuum-tight joint, is hydrogen line **39** which connects through valve **40** to a hydrogen supply (not shown).

The elevating means **32** for the work comprises a solenoid or an electromagnet **41** of generally hollow cylindrical configuration, which is disposed axially about and moves in close proximity to the outer surface of the upper portion **35** of bottle **29** with small clearance, and a suitable power supply (not shown). Inside bottle **29** is provided a magnetic cylindrical work carrier **42**, as an armature for the solenoid **41**, which fits the inside diameter of upper portion **35** also with small clearance and carries a suitable loading hook **43** on its lower face.

Axially aligned within the bottle **29** on the top of an appropriate ceramic supporting table **44** is open-ended container **33**, suitably graphite and half filled with copper **45**. Said container **33** has the appropriate inside diameter and length to permit the complete immersion of the bar **26** within said container. Supporting table **44** is juxtaposed in turn on the upper surface of mounting plate **36**.

Induction heating coil **31** axially surrounds lower portion **34** of bottle **29** with a sufficiently small amount of clearance to insure satisfactory radio frequency coupling between container **33** within said bottle **29** and the coil **31**.

To impregnate bar **26** with copper **45**, the work, namely bar **26** and mounting means **27**, are suspended axially from magnetic work carrier **42** of impregnating apparatus **28** by inserting loading hook **43** of carrier **42** through the loop of mounting means **27**. During the attachment of the work to carrier **42**, it will be understood that the open end of the "Vycor" bottle **29** is held by suitable blocking means (not shown) a sufficient distance above mounting plate **36** so that the elevating means **32** securing said carrier therein by its magnetic field is juxtaposed at the lowest point of its downward travel with respect to the upper closed end portion **35** of bottle **29**. After attachment of the work to the carrier **42**, the electromagnet **41** of the elevating means **32** raises carrier **42** and the work to a position in close proximity to the closed end of the bottle **29**, in order that the graphite container **33** and the copper may be aligned axially on table **44** above mounting plate **36**.

The bottle **29** is then unblocked and its open-end brought into contact with mounting plate **36**. During the downward movement of bottle **29**, the work carrier **42**, through a like movement of elevating means **32**, retains its position near the closed end of the bottle **29** and above the container **33** and any induced field of induction coil **31**. Said bottle **29** is sealed to plate **36** by vacuum putty **37** and the interior of the bottle is evacuated through exhaust pipe **38** and valve **38′** by pumping means **30**.

When the desired vacuum has been obtained, bar **26** is lowered by elevating means **32** partially within container **33**, but out of contact with the copper **45** and all three members, namely bar **26**, container **33** and copper **45** are induction heated slowly by coil **31** to, approximately 1180° C. a temperature 100° C. above the melting point of the copper **45**, in order that said copper will wet the molybdenum bar **26**. At this point molybdenum bar **26** is lowered into the molten copper until said bar is completely immersed, the pumping means **30** is cut off from the bottle **29** by closing valve **38′**, and hydrogen gas at a pressure slightly less than one atmosphere is admitted to the bottle **29** through valve **40** and line **39**. This hydrogen atmosphere prevents oxidation of the molybdenum bar **26** and the copper **45** and forces the molten copper into the interstitial void spaces in the the porous molybdenum bar **26**. After approximately three minutes of contact between the two metals, bar **26**, now impregnated with copper **45**, is withdrawn from the container **33** and allowed to cool in the hydrogen atmosphere. After the impregnated bar **26** is cooled, the hydrogen pressure within bottle **29** is increased above one atmosphere to break the silicone putty seal between bottle **29** and plate **36**. Valve **40** is immediately closed and the work, namely impregnated bar **26** and mounting means **27**, withdrawn from bottle. The mounting means are severed from the bar, as by cutting.

The impregnated bar **26** is rolled, as in the apparatus of Fig. 5, to the desired cross-section of a lead-in conductor such as conductor **8** of Fig. 1 or conductors **14** of Fig. 2. As a result of this rolling method of working the density of the finished lead-in conductor wire is 99% to 100% of maximum theoretical density.

It will be understood that either the sintered bar **20** or the impregnated bar **26** could be rolled into a thin flat sheet which could be die-formed or spun into cup-shaped parts, similar to anode **6** of Fig. 1, and cylinders machined therefrom, similar to grid cylinder **4** of Fig. 1.

It has been found that the composition of the mixture of molybdenum and copper employed in the manufacture of parts for sealing to soft glass, such as cylinder **4**, anode 6, lead-in conductors, such as conductor 8, and conductors 14 for sealing through soft glass, may vary from 40% molybdenum–60% copper, having a coefficient of expansion of 11×10^{-6} in./in./° C. to 80% molybdenum–20% copper, having a coefficient of expansion of 8.8×10^{-6} in./in./° C. This coefficient of expansion range corresponds uniformly with the coefficients of expansion of most soft glasses. For example, several typical soft glasses and their coefficients of expansion are listed in the following table:

Code No.	Corning G. No.	Coefficient of expansion in./in./° C.
G001	1	9.0×10^{-6}
G005	5	8.9×10^{-6}
G012	12	8.7×10^{-6}
887	858V	8.9×10^{-6}

While a specific mixture of molybdenum and copper has been described, it will be understood that other metals probably can be used to make lead-in conductors and parts for sealing to soft glasses. The substitution of silver for copper, and/or the substitution of tungsten for molybdenum are possibilities. Other methods of making mixtures such as wet doping molybdenum oxide with copper salts followed by reduction, pressing, and sintering may be employed. Other methods of working the billet such as swaging, drawing, or extruding said billet to produce lead-in conductors and parts for sealing may be substituted.

Thus it will be seen from the foregoing description that our invention has overcome the defects of the prior art soft glass stems and metal to soft glass seals. We have provided a lead-in conductor, such as conductor 8 of Fig. 1 or conductors 14 of Fig. 2, or a metal part, such as grid cylinder 4 or anode 8 of Fig. 1, for sealing into soft glass, said conductor comprising a mixture of two non-alloying metals which will match the coefficient of expansion of most soft glasses. Specifically, the present invention provides the mixture having a composition

which may vary from 40% molybdenum–60% copper to 80% molybdenum–20% copper. Lead-in conductors and parts for sealing to soft glasses, which are made from such a mixture have a high electrical conductivity, are diamagnetic and have low losses in high frequency devices, and possess the quality of strength and ductility required for shaping and bending.

Although preferred embodiments of our invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

We claim:

1. In an electron tube comprising a soft glass member and a metal member embedded and in direct contact with said glass member, said metal member comprising a mixture of from 40 to 80% by volume of molybdenum and the balance by volume of copper, said mixture having a coefficient of expansion in the range of 8.8×10^{-6} in./in./° C. to 11×10^{-6} in./in./° C.

2. In an incandescent lamp comprising a soft glass member and a metal member embedded and in direct contact with said glass member, said metal member comprising a mixture of from 40 to 80% by volume of molybdenum and the balance by volume of copper, said mixture having a coefficient of expansion in the range of 8.8×10^{-6} in./in./° C. to 11×10^{-6} in./in./° C.

References Cited in the file of this patent

UNITED STATES PATENTS

927,935	Von Bolton	July 13, 1909
1,034,949	Arsem	Aug. 6, 1912
1,477,797	Adams	Dec. 18, 1923
1,552,184	Adams	Sept. 1, 1925
1,809,780	Gebauer	June 9, 1931
1,992,493	Los	Feb. 26, 1935
2,061,755	Cooper	Nov. 24, 1936
2,288,499	Van Horn	June 30, 1942
2,411,523	Chivigny	Nov. 26, 1946
2,490,776	Braunsdorff	Dec. 13, 1949