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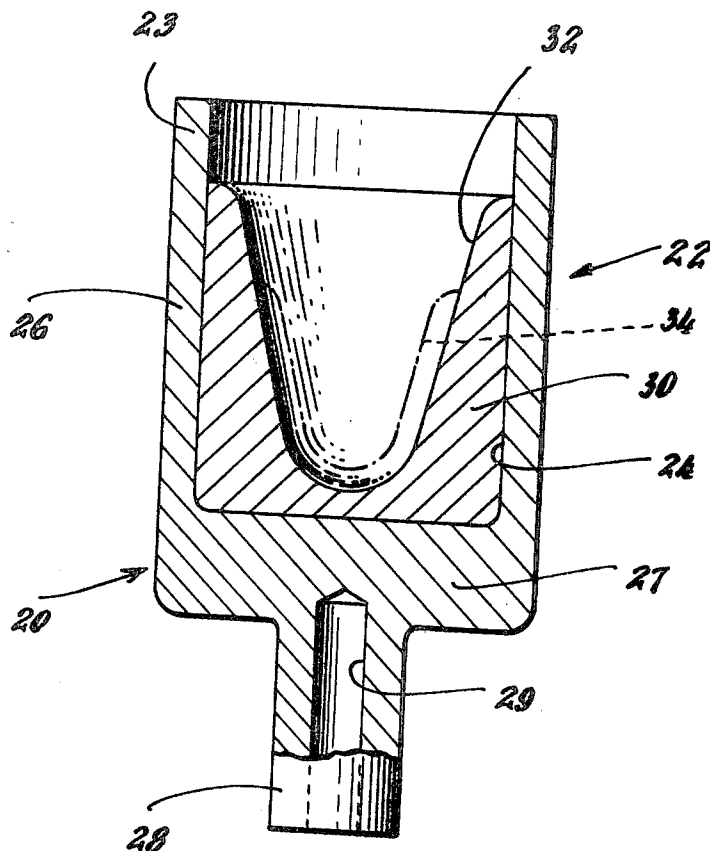
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[54] **ALKALI METAL CATHODE LAMPS**
5 Claims, 1 Drawing Fig.

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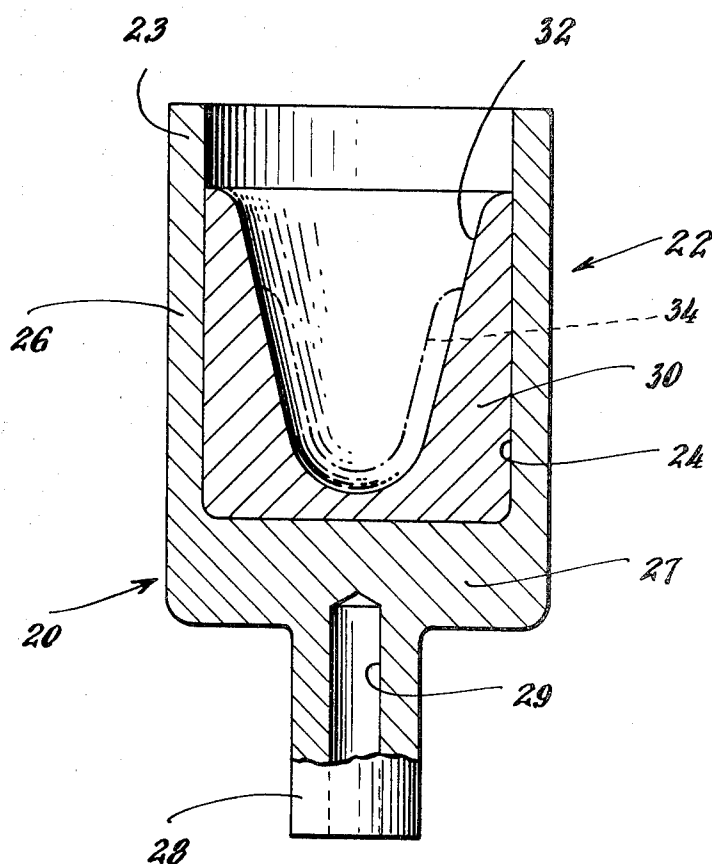
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ABSTRACT: The radiation emitting cathode of spectral source lamps often is a hollow cup, the interior of which contains a coating of the spectrally emitting element or elements. The forming of such a coating of an alloy of an alkali metal (or metals) with, say, tin in the presence of some boron is proposed, resulting in higher melting points and lower vapor pressures, thereby allowing higher operating lamp currents and consequent spectral radiation intensity. The coating material is formed, say, directly on the interior of the cathode cup (say, of titanium) by fusing an alkali metal borohydride with tin, thereby avoiding the need to handle pure alkali metal. The hydrogen gas liberated during alloy formation removes some of the contaminants (e.g., oxides). A boron-containing, glassy slag may be readily separated from the alkali metal alloys. Specific examples in which the alkali metal component is sodium, potassium, or a mixture of sodium and potassium are disclosed. The other metal may be, for example, tin or lead.



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ALKALI METAL CATHODE LAMPS

This invention relates to improvements in hollow cathode lamps of the type used as sources of spectral radiation. More particularly the invention concerns the preparation of hollow cathodes for such lamps, in which the active material on the interior of the hollow cathode holder includes at least one alkali metal.

INTRODUCTION

One type of source of spectral radiation (which is useful in spectroscopic analysis, for example by means of an atomic absorption spectrometer) is the hollow cathode lamp. In such lamps the cathode is cup shaped and includes as at least a substantial portion of its interior surface a material including the element or elements, having the spectral radiation characteristic desired. For those elements having suitable physical characteristics (such as melting point, vapor pressure and electrical characteristics), the spectral element may be, for example, a coating on the interior of a hollow cathode holder of another metal. If the element for which the spectral radiation is desired has, for example, extremely low melting point or high vapor pressure at the operating temperature of the lamp, other techniques must be utilized. One such technique is the formation of an alloy of the desired element (or elements) with other metals.

The alkali metals as a class have very low melting points and very high vapor pressures relative to the normal operating temperature of the cathode of the lamp (around 400° C.). It has already been proposed to use binary alloys of the alkali metals (for example, sodium and potassium) with for example, lead, and utilize the resulting alloy (e.g., NaPb₃ and KPb₄) as the interior surface of a hollow cathode. Such prior technique does not provide a complete solution to the problem in that the resulting binary (sodium-lead and potassium-lead) alloys still have relatively low (approximately 325° C. for NaPb₃) melting points, thereby necessitating relatively low operating temperatures (and therefore both low current and radiation intensity). Additionally the formation of such alloys in situations utilized in hollow cathode lamp production is practically difficult because of the well known problems in handling the extremely chemically active alkali metals.

The present invention greatly facilitates manufacture, in that the materials initially alloyed are both safer and require less expensive apparatus in their handling, both prior to and during the alloying process. Broadly the invention utilizes one or more alkali metal borohydrides and a suitable additional metal (for example, tin) to form an alloy containing the desired alkali metal, some boron, and the additional metal. The resulting alloy also has a somewhat higher melting point and lower vapor pressure at, say, 350° C. than the corresponding binary alloys.

Accordingly, an object of the invention is the provision of a simpler, more economical method of manufacture of a hollow cathode assembly for an alkali metal spectral radiation lamp.

Another object is the provision of a hollow cathode assembly for use in a spectral radiation lamp, utilizing an improved alkali metal alloy as the emitting material.

Other objects, advantages and features of the invention will become obvious to one skilled in the art upon reading the following detailed description in conjunction with the accompanying drawing, in which:

The sole FIG. is a cross section through a hollow cathode assembly of the invention, including an interior coating of the alkali metal, boron, and additional metal alloy.

DESCRIPTION

The drawing illustrates a finished hollow cathode assembly 20 in which a hollow cathode cup holder 22 (of, for example, pure titanium) has a coating 30 of an alkali metal, boron, and additional metal alloy substantially covering the interior surface 24 of both the cylindrical sidewall portion 26 and the heavier bottom portion 27 of the holder. Such conventional

hollow cathode holders are provided with a reduced portion 28 having a recess 29 for engagement with a pin (not shown) of the lamp in which they are used, which pin provides both mechanical support for and the (negative) voltage connection to the cathode assembly. The tertiary alkali metal alloy at 30 may either be prealloyed and then cast within the hollow cathode cup 22, or both the alloying and casting may be done in the same holder 22 intended to be utilized in the finished assembly, as will appear hereinafter.

A general description of how the alkali metal alloy coatings according to the invention may be made is given, followed by three specific examples, utilizing different alkali metals. In the immediately following description the alkali metal will be assumed to be potassium merely for simplicity of expression; as will be seen not only may different alkali metals be used, but even mixtures of different alkali metals.

A small quantity of the alkali metal borohydride (e.g., KBH₄) is positioned at the bottom of a hollow cathode cup (having its reduced end 28 lowermost) or a suitable crucible of similar shape (which crucible may be made for example of graphite). The alkali metal borohydrides (in particular, potassium and sodium borohydrides) are substantially completely stable in dry air at room temperatures (these particular borohydrides have been maintained in (dry) air filled vials for several weeks without any noticeable deterioration through chemical reaction). For long periods of storage, or at elevated temperatures (as in the succeeding manufacturing steps) the borohydrides should preferably be maintained under an inert atmosphere (for example, argon or at least dry air). For short term periods (such as during weighing or other simple manipulative steps), the borohydrides may be exposed to normal ambient air (especially of only moderate humidity) without any appreciable decomposition occurring. A substantially larger (on the order of ten times as much by weight) quantity of relatively pure tin is then placed on top of the alkali metal borohydride, and the entire assembly heated to cause first melting of at least the tin and then decomposition of the alkali metal borohydride in a controlled manner, thereby evolving hydrogen. The inert atmosphere is preferably constantly changed so as to flush away the evolved hydrogen.

A convenient apparatus is an enclosed centrifuge having an external induction heater and having inlet and outlet connections for the constantly flushing, say, argon gas. Constant moderate current is supplied to the induction heater until the tin melts (at 232° C.) completely. The current is then slowly raised until evolution of the hydrogen (indicating the decomposition of the borohydride) starts. The rate of decomposition should be controlled by (manual) adjustment of heater current, or more simply by turning the heater current switch on and off, to avoid violent hydrogen release and the consequent loss of material over the upper edge of the container (e.g., 23 of the illustrated hollow cathode holder). During the entire heating operation the container and its contents are preferably slowly spun by the centrifuge to assist in mixing of the ingredients and escape of the hydrogen gas.

The passage of the hydrogen gas through the molten tin has the desirable effect of reducing any tin oxide which may be present (because of surface oxidation of the tin in its original form). After the bubbling stops (indicating that all of the alkali metal borohydride has given up its hydrogen), the heating current is completely turned off, and the graphite crucible, hollow cathode holder, or other container is cooled. A glassy coating or slag is formed substantially on the upper surface (e.g., at 32) of the alloy, such slag 34 including a substantial proportion of boron compounds. This slag may be readily removed from the metallic alloy (e.g., of potassium, boron, and tin).

Although it is possible to recast the alloy in the same hollow cathode holder (when such is used as the container in the foregoing steps), preferably the alloy is recast into a clean new cathode cup (of titanium for the exemplary alloy) either at this stage or at a later stage of lamp assembly. The desired shape of the final alloy coating at 30 may be obtained either by

centrifuging or by nutating (i.e., turning about a "wobbly" generally vertical axis) the cathode or the lamp into which it has already been installed while the alloy is molten, and then cooling to solidify the coating.

SPECIFIC EXAMPLES

Example I: Sodium

A sodium, boron, tin tertiary alloy may be prepared according to the previous method by utilizing the following specific quantities and conditions. An amount of tin shot in the 0.700 to 0.900 gram range is weighed and an amount of sodium borohydride is placed at the bottom of the, say, graphite container (or titanium hollow cathode holder) in accordance with the following proportions (normalized to exactly one gram of total initial mixture):

	Specific Example	Approximate useful range
Sodium borohydride.....	0.123	0.070-0.165
Tin.....	0.877	0.930-0.835

As previously stated, the container with the sodium borohydride in the bottom and the tin thereover is placed within a flushing inert (e.g., argon) atmosphere. Thereafter heat is supplied to first melt the tin and then to decompose the sodium borohydride (at about 500° C.), moderating the rate of hydrogen evolution to avoid loss of material; the temperature is finally raised slightly to insure a complete melting of the alloy. All of the heating steps are preferably done with the hollow cathode cup or other container being slowly spun by the centrifuge. Upon cooling, the previously noted glassy layer 34 tends to form as a discontinuous dispersion or group of particles over the sodium, boron, tin alloy surface (i.e., 32). These particles may be readily removed by mechanical means (i.e., physical scraping), and the tertiary sodium, boron, tin alloy is then preferably recast in a titanium hollow cathode holder (22) (which may be identical to container as used in the previous steps).

For a total of one gram of initial ingredients (and therefore 0.123 grams of sodium borohydride), approximately 0.014 grams of hydrogen will be released. This much hydrogen would occupy approximately 150 cc. at standard conditions (atmospheric pressure and 0° C. or 273° K) and will occupy somewhat less than 500 cc. at the elevated temperature (approximately 500° C. or 773° K) utilized during the bubbling period. A relatively fast flushing of (say argon) inert gas is therefore preferably used to insure substantially complete removal of the hydrogen gas as a relatively low, safe concentration of hydrogen in the outflow gas.

Example II: Potassium

A similar potassium, boron and tin tertiary alloy may be formed by utilizing an analogous technique, using a somewhat smaller amount (by weight) of potassium borohydride. The following proportion of original ingredients (again normalized to a total of one gram) may be used:

	Specific Example	Approximate useful range
Potassium borohydride.....	0.080	0.050-0.140
Tin.....	0.920	0.950-0.860

The manufacturing steps are substantially identical to the ones given just above for the analogous sodium alloy (and the general explanation preceding Example I). The only two differences are: the slag 34 (containing boron compounds) tends to form a more even coating over the entire upper surface (i.e., 32) of the final alloy, and may still be removed by simple mechanical means; and less hydrogen is evolved per gram of total mixture for the same weight percentage of potassium borohydride, namely, about 65 cc. at standard conditions

(about 185 cc. at 500° C., (773° K)), or about 210 cc. at 600° C. (873°K). Except for the somewhat different scraping procedure of the slag and the somewhat lower inert gas flushing rate useable, the potassium borohydride and, say, tin are processed in the same way to form the tertiary (potassium, boron and tin) alloy and the final coating.

Example III: Sodium-Potassium Mixed Alloy

A sodium, potassium, boron and, say, tin 4-element alloy may be made in an analogous manner to those previously described, for use in a spectral radiation lamp to obtain radiation in the characteristic spectral lines of both sodium and potassium. Such a mixed alkali metal 4-element alloy may be made from the following proportions of starting ingredients (again normalized to a one gram total of reactants):

	Specific Example	Approximate useful range
Sodium borohydride.....	0.062	0.035-0.120
Potassium borohydride.....	0.040	0.025-0.100
Tin.....	0.898	0.940-0.780

The alloying technique is again essentially identical to that of the general description in Example I with the following minor differences. The total amount of evolved hydrogen (and therefore the minimum sufficient inert gas flushing rate) will be intermediate between those of Examples I and II. Similarly although the slag formation is somewhat different in form, removal of these boron compounds is essentially no more difficult than in Examples I and II.

As previously mentioned, during the initial alloying process (for all of the above examples and all analogous alloy formations), the temperature should be carefully raised slightly after the apparent completion of the decomposition (and alloying) of the borohydride (i.e., after bubbling of hydrogen ceases), to insure actual complete consumption of the alkali metal borohydride(s). On the other hand, the temperature should never be raised much above that necessary to cause the particular result desired (e.g., melting of the "additional metal", say, tin; decomposition of the borohydride at moderate rate; and melting of the final alloy during final casting); such moderation in temperature lessens the possible losses of the alkali metal (as vapor) during the various manufacturing stages.

ALTERNATIVES AND CONCLUSION

Although all of the specific examples given above utilize tin as the additional metal, other metals may be used instead. The additional metal should have reasonably satisfactory physical characteristics, the ability to alloy with the alkali metal in the presence of boron, and be free of any spectroscopic interference with the alkali metal(s) spectral line emission. An example of a metal having such properties, which may therefore be substituted for the tin in the above examples, is lead (which has in fact been successfully tried).

In both examples I and II the alkali metals (sodium and potassium respectively) are initially introduced so as to form approximately 4—11 percent (say 6 percent) by weight of the initial ingredients. In each case however a measurable but relatively small amount of the alkali metal is lost in the form of the boron compounds in the slag and perhaps even as lost metal during the alloying process. In general the amount of the alkali metal (i.e., the sodium of Example I, the potassium of Example II and the total of sodium and potassium in Example III) will be reduced from, say, about 6 percent to approximately 2 percent to 4 percent by weight in the final alloy.

Similarly a substantial proportion of the boron is lost (primarily in the slag material) so that its original proportion is probably halved during the manufacturing process. The residual boron, although typically present as only a fractional percentage (by weight) in the total final alloy, nevertheless has an appreciable effect in raising the melting temperature of the alloy (relative to a similar but boron-free alloy) and

moderating the vapor pressure (at, for example, 350° C.) of the alkali metal.

The invention therefore provides a relatively simple technique for providing an alkali metal alloy for a hollow cathode having desirable characteristics (and additionally provides a somewhat improved alloy for this purpose having a somewhat higher melting point and lower vapor pressure than the most closely related previously used alloys, i.e., the binary alloys of the alkali metals without any boron content. The inventive process entirely avoids the handling of the pure alkali metal(s) and the attendant problems and hazards, as well as requiring little equipment. It therefore is particularly suitable for forming relatively small quantities of the alloy, for use, for example, in making only one or a few spectral radiation lamps at a time. The hydrogen (and perhaps the boron as well) released during alloy formation reduces the oxides of the "additional" metal (often present on its surface); in any event elimination of existing oxide from the final alloy has actually been observed when either tin and lead (having some surface oxidation) has been the "additional" metal used.

Although three specific examples involving two alkali metals and a mixture thereof have been specifically described, it will be obvious to those skilled in the art that other alkali metals and mixtures thereof may be used to form the analogous alloys. Similarly other "additional" metals (having the requisite moderately low melting points and other desirable alloying properties, as well as exhibiting no spectroscopic interference with the alkali metal emission) may be utilized besides tin and lead. Further although specific proportions have been given in the Examples, obviously the relative proportions may be varied over a relatively large range. Because of these and other obviously possible variations, the invention is not limited to any of the details of any one or more of the exemplary embodiments specifically disclosed; on the contrary the invention is defined solely by the scope of the appended claims.

We claim:

1. In an improved cathode assembly for use in a radiation source lamp, a cathode holder and a spectrally emitting coating on said cathode holder, said coating being an alloy comprising:

at least one alkali metal selected from the group consisting of sodium, potassium and mixtures thereof in the range of 2 percent to 10 percent by weight of the total constituents of said alloy;

boron in the range of ¼ percent to 4 percent by weight of said total alloy constituents;

an additional metal selected from the group consisting of tin and lead in the range of 86 percent to 98 percent by weight of said total constituents,

said coating thereby being a tertiary alloy having a melting point not only substantially above that of said one alkali metal, namely, sodium, potassium, or the mixture thereof, and of said additional metal, but also somewhat above that of the corresponding, boron-free, binary alloy of said alkali metal and said additional metal; and

whereby an improved cathode assembly, capable of use with higher operating lamp current and therefore capable of production of greater intensity spectral radiation, is obtained.

2. An improved cathode assembly according to claim 1, in which:

said cathode holder is a generally cup-shaped hollow cathode, and

said alloy coating covers a substantial part of the interior surface of the "hollow" thereof.

3. An improved cathode assembly according to claim 1, in which; said additional metal comprises tin.

4. An improved cathode assembly according to claim 3, in which; said cathode holder comprises titanium.

5. An improved cathode assembly according to claim 1, in which; said additional metal comprises lead.

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