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METHOD OF MAKING SINTERED CATHODES

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FIG. 1

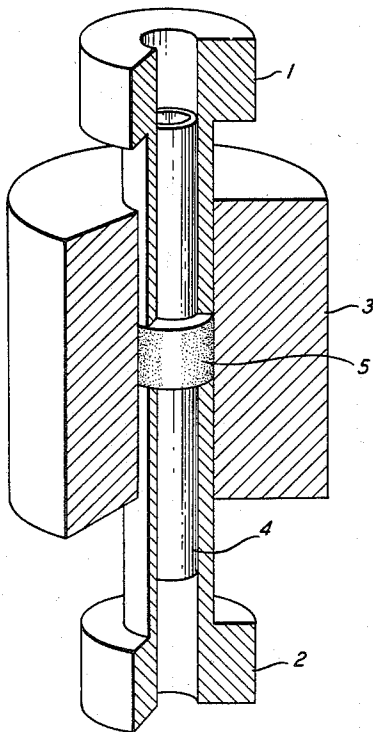
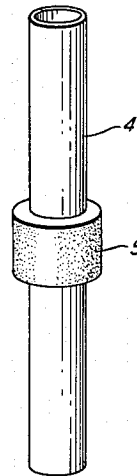


FIG. 2



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METHOD OF MAKING SINTERED CATHODES

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This invention relates to processes for manufacturing molded cathodes for use in electron tubes and to cathodes so produced. Cathodes made in accordance with this invention are extremely rugged, are capable of withstanding a high degree of back-bombardment and may be operated at high emission levels and at relatively high temperatures over long periods of time. These cathodes are particularly suitable for use in high power applications such as in magnetron structures.

With the development of radar, and other high power circuits, there has evolved a need for cathode structures capable of delivering high current densities of the order of 100 milliamperes per square centimeter and up to several amperes per square centimeter at extremely high frequencies of the order of kilomegacycles ranging through the K, X, and S frequency bandwidths. Required characteristics of such cathodes especially for use in magnetron structures include the ability to withstand considerable back-bombardment and the attendant high cathode temperatures without significant loss in emission. Conventional coated cathodes used for low power applications are generally unsuitable for this purpose not only because the cathode base material such as nickel is generally incapable of withstanding high temperature operation due to its high vapor pressure at these high temperatures, but also because the thin emissive layer on such devices breaks down under conditions of arcing and back-bombardment so that emission is very quickly lost.

For these and other reasons high power cathodes in use today may contain as a base material a refractory metal, and are generally manufactured in such manner that the emissive material is caused to penetrate the matrix to a substantial depth so as to provide a reservoir of emissive material available on demand during operation of the tube.

One of the more common cathode structures in use in such high power devices at this time contains a suspension-impregnated porous matrix. In the manufacture of such a device the matrix which may, for example, be primarily tungsten is painted with a suspension of an emissive material under conditions of manufacture which cause some penetration of the emissive material into the matrix by capillary action. Such suspension-impregnated porous matrix cathodes are broadly applied to such use despite severe disadvantages both from a manufacturing and operational standpoint. In manufacture such structures are extremely expensive to make, there being required from 17 to 19 critical processing steps, including the painting of the matrix and subsequent pressing, the latter designed to improve the compactness of the mass. Due to these very involved manufacturing techniques reasonable reproducibility is difficult to obtain.

During operation such suspension-impregnated porous matrices manifest frequent arcing probably due to non-uniform distribution of emissive material on the surface of the matrix. Such arcing probably results in vaporization of emissive material and poisoning of the emissive surface. Magnetron tubes containing such cathodes, when operated at frequencies of the order of kilomegacycles, manifest arcing at the rate of the order of from several hundred to several thousand arcs per hundred hours. This arcing, in addition to deleteriously affecting

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the chemistry of the cathode and setting up a conduction path between the cathode and anode, obscures the pulse signal and results in temporary loss in control of the tube. Such loss of control may be of considerable consequence in pulse-controlled systems.

A further disadvantage in some types of prior art cathodes resides in the very high operating temperature necessary to produce sufficient emission. Operation at such levels, which in some devices is in the order of 1100° C. and higher, necessarily results in a further loss of barium or other emissive material by evaporation and also results in deposition of such material on comparatively cool surfaces within the tube, notably on the anode with resultant loss in configuration and cavity Q, and in loss in conduction of the anode.

A further disadvantage of the requirement of such high temperature operation relates to the practical requirement that the temperature must be produced by a heater within the tube. By reason of the very close spacing generally required, heaters capable of producing such temperatures are generally elongated fine cross-section wires of materials such as tungsten. Such heater configurations are very delicate, and any loss in heater material results in rapid impairment and possible failure.

In accordance with the processes of this invention, there are produced cathodes capable of delivering the required level of emission, that is from one hundred milliamperes per square centimeter to amperes per square centimeter at temperatures as low as the order of 900° C. and lower.

Arcing in the cathodes of this invention may be substantially reduced to well below the order of several thousand arcs per hundred hours down to the range of hundreds of arcs and even fewer than a hundred arcs per hundred hours in magnetron use.

In addition to enjoying the advantages outlined, during operation the manufacturing techniques are considerably more economical and simpler than those techniques used in the manufacture of prior art devices. The cathodes of this invention are manufactured by the use of only three steps thereby making for ready reproducibility of these cathodes.

Briefly the processes of this invention make use of three processing steps: mixing, pressing, and firing. In the mixing step the refractory material going into the cathode which generally contains both molybdenum and tungsten is mixed together with an emissive material such as the single, double or triple alkaline earth carbonates or mixtures thereof and also any activating material which may be desired, the combination of which will break down thermally or upon reduction at elevated temperatures to produce the corresponding alkaline earth oxides. The mixture is then compressed under high pressure of the order of tons per square inch into the desired configuration, after which it is fired, first in a reducing atmosphere at one temperature range during which barium or other alkaline earth oxides are produced, and finally in an inert atmosphere at a higher temperature range under conditions sufficient to produce a compact sintered mass.

The finished cathodes of this invention contain as the predominant material the elemental material of the refractory mix and are of a chemistry such that substantially all of the emissive material is in the active form, that is, is available for use during operation of the tube. Considering barium as the primary emissive material the active compounds present in the processed cathode are barium oxide and basic barium tungstate and/or basic barium molybdate. It is hypothesized that in large part the high level of emission made available at relatively low temperature is due to decomposition of the basic tungstate and/or molybdate in the presence of ele-

mental tungsten and/or molybdenum and any coded reducing agent to release elemental barium, either directly, or indirectly through the oxide mechanism.

Matrices produced in accordance with processes of this invention are homogeneous and contain well-distributed active compounds of emissive material throughout their geometry.

The absence of an excess concentration of emissive material or active compounds containing such material on the surface of the cathode results in an improvement in reproducibility, as compared with suspension-impregnated porous matrices and also results in decreased arcing.

Cathode matrices and support sleeves as prepared herein have substantially identical temperature coefficients of expansion, thereby reducing the likelihood of failure due to thermal stress both during processing and operation, and also making for a good thermal conduction path between the matrix and support structure so as to permit efficient dissipation of heat when generated in the matrix for example by back-bombardment. Devices as produced herein are extremely rugged from a physical standpoint and evidence good bonding between matrix and sleeve thereby further aiding conduction and eliminating shifting and other changes in configuration during use.

The cathode systems herein are comprised of materials which have low vapor pressures at the requisite operating temperatures thereby reducing vaporization at the matrix and accompanying deposition on the anode. Such deposition on the anode is deleterious in that it may affect the geometry of the tube and in that materials so deposited are likely to be of low electrical conductivity thereby further impairing the efficiency of the tube.

Since, in the processing of the cathodes herein, virtually all of the carbonates or other emissive materials comprised of compounds decomposable to yield gaseous products have broken down on firing, the gas evolution rate during operation is very low. High gas evolution is harmful in that gases so evolved may oxidize the cathode materials and ultimately poison the emissive material.

The cathode surfaces as produced in accordance with the processes of this invention are smooth, compact and homogeneous and are therefore machinable if such is desired.

The invention may be more easily understood by reference to the figures in which:

Fig. 1 is a perspective view of a double-acting die suitable for use in the process herein and also depicts a cathode under treatment; and

Fig. 2 is a perspective view of a cathode prepared in accordance with this invention.

Referring again to Fig. 1 there is depicted a double-acting die which may be constructed of a hard tool steel such, for example, as "Ketos" steel which has a hardness of from 50 to 55 on the Rockwell C scale, the die consisting of upper plunger 1, lower plunger 2 and body or die 3. Within the die there is shown a cathode sleeve 4 which may or may not be the sleeve structure to be incorporated in the final tube. In either event cathode sleeve 4 is constructed of a material having a temperature coefficient of expansion similar to that of the cathode matrix. In the processes and products herein, cathode sleeve 4 is commonly made of molybdenum. Within die 3 and about the cathode sleeve 4 there is shown a cathode structure 5 under processing. As is evident from the drawing, pressure is applied to cathode 5 through plungers 1 and 2.

In Fig. 2 there is depicted a cathode 5 about a cathode sleeve 4. At this stage in the processing cathode 5 and sleeve 4 have been removed from the double-acting die of Fig. 1. If the process under study is one in which cathode sleeve 4 is the ultimate support structure for the cathode 5, Fig. 2 may depict the structure in any

stage of processing after removal from the die and up to and including insertion in the tube.

Reference will be made to Figs. 1 and 2 in the general outline of the processes of this invention which follows.

The initial step in the preparation of a molded cathode in accordance with this invention is the preparation of the emissive mixture. Powders used in this step generally contain at least of the order of ten or twenty percent of a particle size of 5 microns to 20 microns or less. In the preparation of the mixture, powders of metallic molybdenum and metallic tungsten are first mixed, the weight ratio being preferably in the range of from 25-75 to 75-25, a mixture of about 50 parts of each material having been found to be ideally suitable in the practice of this invention. Emissive mixes have also been made up in which the metallic materials used were solely molybdenum, and also solely tungsten. It has been found that although no physical disadvantages are introduced by the omission of one or the other of these refractory materials, the resultant cathode has a somewhat lower emission than does one made up from a combination of the two materials. It should be noted, however, that the chief advantage of the invention herein is not improved primary emission which, however, is more than adequate for the intended purposes, but resides rather in the ease of manufacture of the cathode and in the very good physical characteristics such as homogeneity of the structure, thermal conductivity and good adherence between the cathode and sleeve. The somewhat lower emission resulting from the use of pure molybdenum or tungsten may, therefore, not be a deterrent to the use of such a cathode for heavy duty applications such as in magnetron structures, where failures of prior art devices to meet specifications have frequently not been due to loss of or to inadequate emission, but have been due to physical breakdown.

Other refractory materials having the requisite refractory and expansivity characteristics such, for example, as thorium and platinum may be included in the mixture, although for reasons which will be discussed it is a requirement of this invention that any such refractory mixture contain some molybdenum or tungsten, it being considered that any refractory mixture suitable for use in the processes of this invention should contain at least 25 percent by weight of either molybdenum or tungsten.

The refractory materials having been thoroughly mixed, for example, by mixing dry in a mortar and pestle for a period of about ten minutes, an emitting mix is then made up by adding to a portion of the refractory mixture a material which will decompose to produce the oxide of a low work function material such as barium and also a small amount of an activator (or reducing material) such as zirconium hydride, silicon, titanium, carbon or other activator materials having similar characteristics known to those versed in the art. Materials included for the purpose of producing emission include the carbonates, nitrates, basic tungstate and basic molybdate of barium, strontium and calcium or mixtures thereof such as strontium carbonate, calcium carbonate, barium carbonate, barium-strontium carbonate, barium-strontium-calcium carbonate and also include the alkali earth salts of unsubstituted mono and polycarboxylic acids such as barium formate. Proportions of these materials which have been found suitable are 89¾ percent of refractory mix, one-quarter percent of zirconium hydride or other activator material and 10 percent of barium carbonate or other emissive material all amounts being in terms of weight percent. Ranges of activator and emission materials have been determined and are discussed in terms of weight percent of emitting mix. Use of zirconium hydride or other activator material in the emissive mixture is well known as is the effect of such an agent. Since the purpose of this material is to reduce the barium oxide or other final emissive material containing compounds pres-

ent in the cathode to the metallic material, and since this reduction may be brought about to some extent by the molybdenum or tungsten or any of a number of impurities contained in the cathode, workable cathodes may be prepared in accordance with this invention from a mixture containing no zirconium hydride or other deliberately added activator material. Some activation is, of course, introduced by the use of very minute amounts of such materials, it having been found, for example, that the use of only one-quarter percent by weight of zirconium hydride has the effect of increasing the emission of the final cathode of the order of 500 percent over a cathode prepared from a mixture containing no zirconium hydride or other deliberately added activator material. While an increase in the amount of activator material results in a further improvement in emission of the final structure, a leveling off point is reached at inclusion of one-half of one percent of activator in the mixture, increasing the amount of zirconium hydride from one-quarter to one-half percent having been found to result in an increase in emission of only about 20 percent. On the other hand, it has been found that increasing the amount of activator material present in the emissive mix above one-half percent may result in adherence difficulties and a consequent deficiency in heat transfer by conduction between the cathode and support.

The range for the amount of emissive material included in the mix is a compromise between the level of emission of the final structure and a mismatching in temperature coefficients of expansion between the cathode and the support, it having been found that for general use in magnetron structures a range of from 5 to 15 percent and a preference for about 10 percent is indicated. It should, however, be noted that whereas the upper limit of 15 percent is a very real limitation, adherence difficulties being introduced above this amount, the lower limit may be further decreased where the accompanying decrease in emission is not objectionable.

To the mixture of the refractory material, the activator material and the emissive material containing compound, there is next added a suitable lubricant in a solvent in an amount sufficient to result in excess liquid. Lubricants suitable for this purpose are well known and include many waxy materials such as paraffin. A solution of stearic acid in ether has been found satisfactory for this purpose, about one percent by weight of the total mix being added. The lubricant such as the stearic acid is sometimes referred to as a "fugitive binder" since it remains during the pressing technique, but escapes during firing.

Having added a lubricant solution the wet mixture is then stirred until dry in a mortar and pestle, it having been found that with the amount of lubricant indicated a period of about 35 or 40 minutes is sufficient for this mixing procedure.

The material having been mixed in a mortar and pestle it is next mechanically mixed for a period necessary to insure homogeneity as by ball-milling for a period of 24 hours or more. For the process steps set forth in the attached examples a Fisher-Kendall type of mixer was found to produce virtual homogeneity in a period of about 72 hours with a 10-gram sample.

The emissive mixture is now ready for pressure molding. The type of molding equipment to be used is dependent on the desired configuration. Regardless of the configuration it is necessary to apply sufficient pressure to result in a compact mass. As a lower limit it has been found that in the case of cylindrical geometry systems the minimum pressure to be applied should be of the order of 20 tons per square inch for a particle size of the order of 10 microns since pressures below this value generally result in nonuniformity of the cathode. With smaller particle size somewhat lower pressures are sufficient since the mass compacts more readily. For example, for a mix containing particles of which

ten percent or more are of a size of 5 microns or less, applied pressures as low as 15 tons per square inch result in reasonably uniform distribution. In general, increasing the pressure applied is helpful over a reasonable range and is not harmful even when this range is exceeded. The upper limit on the range is generally dictated by some consideration other than that of the characteristics of the cathode itself. For example, if an annular-shaped cathode as cathode 5 in Fig. 1 is to be produced and if the support structure is tubular as is cathode sleeve 4 in that figure, it is found that increasing the applied pressure above about 50 tons per square inch results in distortion of the sleeve. Where the cathode matrix is to be molded in a planar shape, such as a disc, pressures as high as 100 tons per square inch and higher may be applied. It has been found, however, that there is little advantage gained in applying pressures greater than from 40 to 50 tons per square inch regardless of the configuration for a particle size of 10 microns since the particles themselves are virtually incompressible over such a range of pressures so that no gain in compactness results when this range is exceeded. Theoretically, of course, any increase in compactness results in an accompanying decrease in the rate of migration of the emitting material through the matrix during processing and operation of the final tube structure. Where the desideratum is ruggedness rather than high emission, as it generally is in the manufacture of the magnetron cathode, a large decrease in migration rate of emissive material through the matrix may be tolerated.

In using a double-acting die such as that depicted in Fig. 1 in the preparation of a cathode such as cathode 5 shown in that figure, bottom plunger 2 is first inserted in die body 3 after which sleeve 4 is inserted onto plunger 2 to the position shown in Fig. 1. A portion of the emitting mix as prepared above is dumped into die body 3 about sleeve 4 after which top plunger 1 is inserted and pressure is applied by means, for example, of a hydraulic laboratory press. In the specific examples appended hereto in which an annular cathode having inside diameter .170 inch, outside diameter .209 and length .240 inch was being prepared, a sample of 306 milligrams of the emitting mix was used. The pressure used was of the order of from 30 to 40 tons per square inch.

The next step in the processing of the cathode is the preliminary firing step which is carried out in a dry atmosphere of a reducing gas such, for example, as hydrogen, methane, ethane or propane. In any event it is necessary that the atmospheric gas contain a minimum of water vapor. A suitable readily available reducing gas for use in the preliminary firing step is prepurified hydrogen, further dried, however, by passage through an electro-dryer utilizing activated aluminum and a catalyzer as a drying medium. The primary objective of this preliminary firing step is to break down barium carbonate or other emissive material-containing compound to the corresponding oxide while producing a minimum of oxidized molybdenum or tungsten. Basic alkali earth tungstate and molybdate may also be formed during this first firing.

The temperature range of the first firing step is from about 700° C. to about 750° C., the lower limit being set by practical considerations since a further decrease in temperature results in the need for an increase in firing time. Increasing the temperature to above about 750° C. is, however, harmful since the resultant increase in rate of breakdown of the carbonate may result in the evolution of carbon dioxide in addition to the water vapor and carbon monoxide normally liberated. Evolution of carbon dioxide is harmful since it is an oxidizing gas and will result in the further oxidation of molybdenum and tungsten. The formation of excessive amounts of oxides of molybdenum and tungsten results in reaction of these oxides with emissive oxides such as barium oxide to form non-emissive normal barium

tungstate or molybdate thereby tying up permanently the barium oxide needed to obtain an emissive cathode.

During the first firing step, it is likely that a small amount of molybdenum oxide and tungsten oxide may form and may be combined to form the eutectic composition. Although the formation of such oxides should generally be kept to a minimum, if such oxides do form, however, it is considered likely that the formation of any oxide eutectic between these materials and its subsequent reduction to the metallic state, should that occur, is desirable in that it may aid bonding and thereby result in a sturdier cathode. This advantage is of course not gained if the original refractory mix contains only molybdenum or tungsten.

Although it is desirable to raise the cathode to its first firing temperature by placing it in a furnace and changing the atmosphere in the furnace to pure dry hydrogen and then raising the temperature of the entire furnace from room temperature up to the firing temperature such a procedure does not generally lend itself to quantity production since a time delay and thermal inefficiency is introduced both in increasing and decreasing the temperature of the furnace. A preferred procedure in quantity production is to place the cathode together with its support structure in a boat which may, for example, be constructed of molybdenum, and to introduce the boat together with the structure into a furnace such, for example, as a quartz tube Global furnace constantly maintained at the desired firing temperature. Where the temperature of such a furnace is maintained at about 750° C., it is found that a rate of introduction of the structure into the furnace of the order of one inch per minute results in no significant flaws due to thermal stress. The apparatus is arranged in such manner that the atmosphere to which the structure is exposed is completely converted to pure dry hydrogen or other reducing gas prior to its introduction into the hot zone of the furnace.

The time of firing is dependent upon the temperature and generally ranges from about 15 minutes to about 2 hours. For a temperature of the order of 700° C. an exposure of from 1 to 2 hours is generally required while at a temperature of about 750° C. an exposure from about 15 minutes to about 30 minutes is adequate. In general, increasing the time of exposure of the order of two to four times is of some advantage in improving omission where greater emission is desired. Further prolongation is generally neither harmful nor advantageous.

After the structure has been fired it is withdrawn from the furnace again at a rate sufficiently slow so to avoid introduction of any substantial imperfection due to thermal stress, it being found that a withdrawal rate of the order of 1 inch per minute is satisfactory. In order to assure a complete pure dry hydrogen atmosphere at all temperatures substantially above room temperature, there is a cooling tube attached to the furnace, the cooling tube containing a moving hydrogen atmosphere. In general, it has been found that a hydrogen rate of about 1.05 liters/min./in.² of cross sectional area is sufficient both to prevent the introduction of air and to remove water vapor and carbon monoxide which evolves during firing.

Although it is not definitely known what reactions take place during first firing, possible reactions are listed below.

- (1) $\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2$
- (2) $2\text{CO}_2 \rightarrow \text{O}_2 + 2\text{CO}$
- (3) $2\text{W} + 3\text{O}_2 \rightarrow 2\text{WO}_3$
- (4) $\text{BaCO}_3 + \text{WO}_3 \rightarrow \text{BaWO}_4 + \text{CO}_2$
- (5) $3\text{BaCO}_3 + \text{W} \rightarrow \text{Ba}_3\text{WO}_6 + 3\text{CO}$
- (6) $3\text{BaO} + \text{WO}_3 \rightarrow \text{Ba}_3\text{WO}_6$
- (7) $\text{BaO} + \text{WO}_3 \rightarrow \text{BaWO}_4$
- (8) $6\text{BaO} + \text{W} \rightarrow \text{Ba}_3\text{WO}_6 + 3\text{Ba}$

For simplicity, all reactions are in terms of tungsten and barium carbonate. The last six reactions may also

occur with the substitution of molybdenum or other refractory material for the tungsten. Substitution of other listed emissive material-containing compounds may also be made. It is generally desirable to proceed at a sufficiently slow rate during first firing as has been indicated to avoid the evolution of carbon dioxide. Over the range of firing temperatures indicated reactions 5, 6 and 8 or any one of them appear to be favored, since analysis has revealed the presence of the basic tungstate and molybdate. The basic tungstate and molybdate are active, and probably under the influence of the presence of metallic tungsten and/or molybdenum break down during processing and tube operation to release elemental barium thereby acting as a reservoir furnishing emitting material as the reserve is depleted. The normal tungstates and molybdates, on the other hand, are not active so that any emitting material tied up chemically in such a compound is lost.

The first firing results in a slight expansion of the cathode matrix so that it may be removed from the support structure if such is desired. If it is so removed it is now placed on the final sleeve to be used in the finished tube. In either event, it is now necessary to position the matrix on the support before proceeding to the second firing step.

Although it is desirable to carry out the second firing step so that exposure to air is avoided between firings, this procedure is generally not commercially feasible. In any event, it has been found that exposure to air after the first firing step does not deleteriously affect the cathode. The second firing may be carried out in a furnace apparatus similar to that used in the first firing step. However, because of the higher temperature which is attained during the second firing step, the quartz tube furnace is unsuitable and an Alundum tube apparatus is substituted. Heating may be produced by one or more Globars. The second firing step is carried out in an inert atmosphere, prepurified nitrogen which has been further dried over activated alumina in an electro-dryer having been used for this purpose. Other inert gases which are available in sufficiently pure form suitable for this purpose after further drying include argon and helium. The presence of reducing gas is to be avoided during second firing since this may result in further breakdown of the emitting oxides to the elemental material thereby making a considerable portion of the emissive material available at one time and decreasing the lifetime of the resultant tube. Additionally, use of a reducing gas during second firing appears to result in a further deleterious reaction so that structures prepared in this manner have lost virtually all of their emission before use.

One of the primary purposes of the second firing step is to sinter or bond the entire mass into a rugged structure. In view of this primary objective little is required of this step other than that the temperature of firing and time of exposure be such as to produce adequate sintering. Purely for practical considerations, a lower limit of about 1300° C. is placed on this firing step, the corresponding minimum time of exposure being of the order of 6 hours and longer. At 1350° C. an exposure of from 4 to 6 hours is adequate, at 1400° C. the minimum period is reduced to from 2 to 3 hours while at 1500° C. an exposure of 30 to 60 minutes has been found to be sufficient, although there is no objection to raising the temperature of second firing to above 1500° C. and up to about 2600° C. at which temperature the melting of molybdenum would cause flow. At this time, however, a temperature of 1500° C. is virtually the maximum temperature available in a commercial furnace operating with a nitrogen atmosphere. During firing the cathode matrix is bonded to the sleeve which, as has been stated, may be constructed of molybdenum or other coexpansive refractory material. If the time of second firing is insufficient to produce a good matrix

to sleeve bond poor thermal conductivity between the two members results. Such a condition makes it more difficult to raise the temperature of the matrix to its operating temperature and during magnetron operation makes it difficult to remove excess heat from the matrix caused by back-bombardment. Generally, increasing the time of exposure during the second firing substantially above the limits indicated is of no advantage. However, increasing the time of exposure of the order of a magnitude or more may result in increasing breakdown of the emissive oxide and may thereby decrease the life of the final tube. In view of the higher temperature of the second firing step, it has been found necessary to introduce the cathode structure into the hot zone of the furnace at a rate which is relatively slow compared with that of the rate of introduction during first firing. An introduction and also withdrawal rate of the order of one-quarter of an inch per minute has been used successfully.

After removal of the structure from the furnace, this element of the tube is essentially completed. All that remains is to complete the structure in accordance with any methods now used in the manufacture of such tubes. The element may then be preactivated if such is required, or may be placed in the tube, sealed onto a pump station and activated in accordance with conventional procedure. The details of preactivation, if desired, and activation although not set forth herein, are well known to those skilled in the art. Final magnetron tube structures in which the cathodes of this invention are usable are also well known, see for example J. B. Fisk, H. D. Hagstrum, and P. L. Hartman, "Microwave Magnetrons," Radiation Lab Series #6, McGraw-Hill, New York (1948).

As has been indicated analysis of several cathode structures prepared in accordance with the procedure outlined above have the characteristic in common that they contain basic barium tungstate and basic barium molybdate. It has also been demonstrated that such cathodes contain the eutectic of molybdenum oxide and tungsten oxide and the reduced resulting alloy. It is believed that the basic barium tungstate and basic barium molybdate act as a reservoir of emissive material during operation of the resultant tube in that both compounds break down probably under the influence of elemental molybdenum and tungsten and any other activating agents to produce elemental barium which then migrates to the surface of the cathode by a diffusion mechanism and is thereby made available. The ruggedness of the structure and capability to withstand high temperature operation are considered to be due primarily to the excellent bonding between the matrix and the sleeve and to the excellent sintering of the material of the matrix itself, both of which make for good thermal conductivity between the matrix and the sleeve, thereby avoiding undue thermal stress. Coexpansivity of the sleeve material and matrix material are, of course, also an essential attribute without which manufacture and operation of the tube would be extremely limited.

By way of further description of the processes of this invention, four specific examples are presented below. In the first of these, the initial emissive material was in the form of barium carbonate. Since the cathode structure so prepared was actually utilized in a magnetron structure, specifically of the 4J52 configuration, operating characteristics of this tube are also given. For the testing of cathodes, once the physical properties are known, it is however convenient to test the cathode in a diode structure. This was done as set forth in Example 2, with a structure as produced in accordance with Example 1, and the characteristics in this use indicated a sufficiently high emission level for use in a magnetron structure. The third example herein makes use of barium strontium carbonate, a well-known substitute for the single carbonate. Since the physical properties of the structure were already known it was considered adequate to test

the second cathode in the diode structure. The operating characteristics of this diode are presented in Example 3.

Example 4 describes an alternate procedure wherein the sole initial emissive material-containing compound or compounds are basic molybdates and/or tungstates of alkali earth metals.

With such a starting mixture, since little or no gas is evolved during firing, the first firing may be dispensed with. Further, probably since the opportunity for oxidation of refractory material is diminished due to non-evolution of water and carbon dioxide during firing, it is found that adequate sintering and bonding to the sleeve is obtained with shorter time or lower temperature of firing although use of the times and ranges set forth above are not generally harmful.

Adequate bonding is obtained at temperatures as low as 1300° C. for fifteen minutes or less. It has also been found that the weight percentage of such emissive compound in the emitting mix may be as high as 25 percent without deleteriously affecting the physical characteristics of the cathode. All other limits are the same as for the above. Activating material may or may not be included in the initial emitting mix.

Example 1

A refractory mixture of 8.98 gms. was made up using 4.49 gms. of molybdenum and 4.49 gms. of tungsten. The materials were mixed dry in a mortar and pestle for a period of ten minutes. The size of the molybdenum and tungsten particles was of the order of 10 microns. To the refractory mix so produced was added 1.0 gm. of barium carbonate and 0.025 gm. of zirconium hydride, both of a 10 micron particle size. These materials were mixed in a mortar and pestle for a about ten minutes after which there was added to this mixture a solution consisting of 0.1 gm. of stearic acid in 5 ml. of ether. The amount of stearic acid solution added was in excess of that absorbed by the mixture so that the resultant mixture at this stage was mushy. Mixing was then continued until most of the ether had evaporated, leaving behind the stearic acid so that the mixture was dry to appearance. This took about forty minutes. The emitting mix was then mechanically mixed for a period of 72 hours.

306 mg. of the mixed powder was then introduced into the annular space about a tubular molybdenum sleeve in a double acting die such as that shown in Fig. 1, and a pressure of 40 tons per square inch was applied by means of a laboratory hydraulic press.

The pressed matrix together with the tubular molybdenum sleeve was then placed in a molybdenum boat and was introduced into a quartz tube furnace containing a moving pure dry hydrogen atmosphere, the furnace being maintained at a temperature of 750° C. Introduction of the boat into the hot zone of the furnace was via an unheated cooling chamber in which there was also maintained a moving atmosphere of pure dry hydrogen, introduction being at the rate of about 1 inch per minute. The boat containing the matrix and sleeve were left in the furnace at the said temperature of 750° C. for a period of 30 minutes after which the boat together with its contents was withdrawn out of the hot zone of the furnace through the cooling chamber again at a rate of about 1 inch per minute.

The matrix having expanded during the preceding firing step it was then removed from the molybdenum sleeve and was placed on the final cathode support structure which was also tubular in shape and composed of molybdenum. The matrix and new sleeve were next placed in a molybdenum boat which was introduced at a rate of about ¼ inch per minute through a cooling chamber into an Alundum tube Globar furnace both containing a moving atmosphere of pure dry nitrogen, the furnace being maintained at a temperature of 1500° C. The boat was left in the furnace for a period of 60 minutes and was then withdrawn with its contents from the fur-

nance through the cooling chamber at a rate of 1/4 inch per minute.

Both moving atmospheres in the two preceding firing procedures were produced by 1.05 liters per minute per inch square cross section flow of gas. Both gases were of the prepurified grade and had been passed through a subsequent drying procedure during which residual water vapor was absorbed by activated alumina in an electro-dryer.

The matrix and support sleeve were then placed in a 4J52 magnetron tube configuration. The tube was placed on a pump station and activation was carried out with the tube maintained at 450° C. for a period of 24 hours, the cathode temperature being raised to a temperature of 1150° C. for the final hour of the activation procedure. The tube was then sealed and was inserted into APS 23 test equipment.

The resultant tube was operated in the said APS 23 circuit which is an expanded fixed frequency radar system. Operation was continuous for a period of 1781 hours with the tube in full operation at an impressed frequency of 9420 megacycles and at a cathode temperature of approximately 875° C. Significant operating parameters, all of which were well within the required limits for magnetrons, are indicated below. The frequency varied from an initial value of 9402 megacycles through a maximum of 9420 megacycles after about 500 hours and to a terminal value of 9417.9 megacycles after 1781 hours. Percentage of missing pulses with a 3/4 microsecond pulse under matched load conditions ranged from an initial value of 0.06 percent through a maximum of 7.6 percent to a terminal value of 0.04 percent. For the same pulse length under mismatch conditions of about 50 percent (considered to be the maximum mismatch encountered in ordinary use) the percentage of missing pulses ranged from an initial value of 0.78 percent through a maximum of 10.4 percent to a terminal value of 0.85 percent. For design purposes, a value of 20 percent of missing pulses is considered to be tolerable. The value of Q_0 which is equal to the energy stored in the cavity per cycle divided by the energy dissipated in the cavity per cycle and which is, therefore, a measure of changes in cavity Q produced, for example, by volatilization of material at the cathode and subsequent deposition on the anode range from an initial value of 665 through a maximum of 700 to a thermal value of 685. Since a change of 10 percent or more may be tolerated, the indicated variation is considered to be excellent.

Example 2

A matrix was prepared using the same starting materials and under identical processing conditions as set forth above.

The resultant matrix together with its support sleeve was placed in a diode structure consisting of said cathode and a nickel anode in such configuration that cathode anode spacing is .055 inch with heater inserted in cathode support sleeve. This assembly was supported within a vacuum system. The diode was then operated at a temperature of 900° C. with a pulse voltage of 3000 volts, a pulse length of 40 microseconds and a repetition rate of 60 cycles per second.

The emission level of the cathode under the above conditions was 400 ma./cm.².

Example 3

Substituting barium strontium carbonate for the barium carbonate of Example 1, identical amounts, materials and processing conditions were used in the preparation of a cathode and sleeve structure. This cathode structure was then placed in a diode as in Example 2 and was operated under the conditions set forth in that example.

The emission level of the cathode was about 360 ma./cm.² at 900° C.

Example 4

Substituting basic barium tungstate for the barium carbonate of Example 1, ten percent by weight without activating agent was used and preparation of the cathode and sleeve structure was identical except that only one firing was used. This firing was in nitrogen at 1350° C. for 15 minutes. The cathode was then placed in a diode as in Example 2 and was operated under the same conditions set forth in that example. The emission level of the cathode was about 100 ma./cm.² at 900° C.

For simplicity the invention has been described primarily in terms of a barium carbonate emitter material containing compound, zirconium hydride activated material and a 50-50 molybdenum-tungsten refractory mix. It has been indicated, however, that substitutions and variations in amount may be made during processing. In one instance relative to the activating agent it has been noted that such material may be omitted in its entirety from the initial mix. It is believed that these variations in the process represent well established substitutions and understandable variations in amount in view of the teaching contained herein. Other variations in the processing steps set forth will suggest themselves to those skilled in the art. Any such variations may be made without departing from the scope of this invention.

What is claimed is:

1. A method of making a cathode for an electron tube comprising making a powder mixture comprising from 5 to 15 percent by weight of a compound of an alkali earth metal which will decompose thermally to produce the corresponding oxide of the alkali earth metal, remainder a refractory material containing at least 25 percent by weight of an element selected from the group consisting of molybdenum and tungsten, pressing the resultant mixture under pressure of at least several tons per square inch, firing the pressed mixture in a reducing atmosphere at a temperature of from 700 to 750° C. for at least 15 minutes and firing in an inert atmosphere at a temperature of at least 1300° C. for a period of at least 15 minutes.

2. The process of claim 1 in which the said refractory material contains at least 25 percent by weight of elemental tungsten and at least 25 percent by weight of elemental molybdenum.

3. The process of claim 1 in which the said refractory material contains molybdenum and tungsten in the weight percentage range of from 25-75 to 75-25 and in which the said compound of an alkali earth metal is a compound selected from the group consisting of barium carbonate, strontium carbonate, calcium carbonate, barium nitrate, calcium nitrate, strontium nitrate, and a salt of an alkali earth metal and an acid selected from the group consisting of the unsubstituted monocarboxylic and polycarboxylic acids and mixtures thereof.

4. The process of claim 3 in which the said refractory material contains approximately 50 percent by weight of molybdenum and approximately 50 percent by weight of tungsten and in which the said compound of an alkali earth metal is a carbonate.

5. The process of claim 1 in which the pressed material is first fired in hydrogen in the said temperature range for a period from 15 minutes to 2 hours and in which subsequent firing in an inert atmosphere is in nitrogen at a temperature of about 1500° C. for a period of at least about 1 hour.

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