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METHOD OF PREPARING EMITTER SURFACES

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This invention relates to methods of preparing emitter surfaces of electron tubes and particularly to surfaces that are designed to provide a high secondary emission. In certain electron tubes it is desirable to provide surfaces having a high secondary (delta) emission. Electron tubes of this character include multiplier tubes, and certain photoelectric tubes. The secondary emission (delta emission) of an electron tube surface may be described as that property which enables a surface to emit electrons when the surface is bombarded with electrons from another source. Certain surfaces have the property of emitting a great many more electrons from the surface than are received in the initial bombardment and it is feasible to designate a "secondary emission ratio" which is characteristic of a particular surface. The secondary emission ratio is the ratio of the number of electrons given off by the surface to the number of electrons received. This ratio is usually more than one, and in respect to some surfaces is a large number, very much greater than unity. Other surfaces have very low secondary emission ratios, and accordingly cannot be used for purposes where secondary emission is desired. It has been discovered that a magnesium oxide film on the surface of a magnesium-silver alloy will provide a high secondary emission ratio, but the preparation of such magnesium oxide surfaces and manufacture and use thereof in tube structures has been accompanied by much difficulty. For example, where such secondary emission surfaces of magnesium oxide have been prepared with the use of oxygen, it has been necessary to prepare the surfaces in a separate tube and then transfer them to the tube in which they are used. The transfer operation is difficult and usually results in degradation to varying and uncertain degree of the properties of the surface.

If the preparation of the secondary emission surface is carried out in the tube where it is used, using an oxygen atmosphere, unwanted oxidation of other tube parts may occur.

It is an object of the present invention to provide an improved method of preparing magnesium oxide films on the surface of components made from magnesium alloyed with silver or other metals. It is a further object to provide a convenient method such that such secondary emission surfaces may be used freely and with reproducible results for commercial and other purposes. It is another object of the invention to provide an improved method of making secondary emission surfaces capable of being utilized at low cost, and by unskilled employes. It is a further object of the invention to provide an improved method of making secondary emission surfaces of constant quality and easily reproducible values.

Other and further objects of the invention therefor will become apparent as the description proceeds.

In carrying out the present invention there may be utilized an alloy composed of magnesium and some other

metal which, for convenience is called the "solvent metal." As the solvent metal which is alloyed with magnesium there is preferably used silver, but gold or copper may also be used. The solvent metal with which the magnesium is alloyed should be one in which the magnesium is reasonably soluble and which is lower on the electromotive scale than nickel, which is commonly used for the supporting structures within electron tubes. Nickel is used for the latter purposes because it has very desirable working qualities, it may be welded, shaped, rolled, and has good out-gassing properties.

In carrying out the invention I may therefore use an alloy composed of a solvent metal and magnesium, for example an alloy of silver and magnesium or an alloy of gold and magnesium, or of copper and magnesium. A silver magnesium alloy containing from one to five percent of magnesium is suitable. Other ranges of magnesium percentage may be used. In certain of my experiments I have utilized, by way of example, an alloy containing 1.7 percent magnesium in silver.

This alloy in sheet form is used for the preparation of the secondary emitter surface. The sheet is first polished with fine aluminum oxide powder or other abrasive powder so as to provide a very smooth and oxide-free surface. The polishing may be carried out by sprinkling a small amount of the abrasive powder on filter paper and working this against the sheet. After the polishing process the alloy sheet is cut and formed into suitable sizes and shapes which will depend upon the particular design of the tube being constructed, and these are then de-greased with any suitable de-greasing agent such as acetone. The acetone is then blotted off with filter paper.

The polished and de-greased sheet cut to appropriate shape is then mounted in the tube structure along with the other tube components, and sealed in an envelope provided with a tubulation for evacuation. The envelope is then evacuated and simultaneously baked. In this procedure the pressure is reduced until it drops to less than 1×10^{-6} mm. of mercury and the tube is then baked. The baking is carried out in a step-wise manner, the temperature being gradually brought up to around 450° C. The temperature is raised gradually so that pressure does not at any time exceed 1×10^{-4} mm. of mercury at any time. The baking is discontinued when the pressure again falls to less than 1×10^{-6} mm. of mercury at a temperature of around 450° C.

The structure may then be permitted to cool.

At this juncture the formation of the magnesium oxide film can be initiated. I have discovered that oxidation of the magnesium can be accomplished by subjecting the magnesium which is exposed on the surface of the alloy sheet to an atmosphere of carbon dioxide. The reaction is thermodynamically exothermic according to the following equation:

$$Mg+CO_2=MgO+CO$$

The carbon dioxide is not harmful in the tube, and the carbon monoxide which is given off in the reaction, is present in only negligible proportions, and does no harm in the amounts present. Indeed, some partial pressure of carbon monoxide is desirable when the tube contains nickel components, as is usual. This is explained hereinafter.

Since the reaction by which the magnesium oxide film is formed in exothermic, such reaction would theoretically proceed by itself, once initiated, but as a practical matter, only small amounts of heat are produced in the reaction, and the heat drain by radiation and conduction stops the reaction if temperature is not otherwise maintained.

There is no theoretical lower limit of temperature for initiating the reaction, since the pressure of CO_2 may be as desired, but as a practical matter, in order to carry out the reaction seasonably, I prefer to heat the alloy sheet to a temperature of say above 400° C. Hence the film formation may proceed directly, after bake-out, without an intermediate cooling. Even at 400° C. the reaction is slow and I prefer to use a somewhat higher temperature, as it reduces the time of formation.

The upper limit of temperature of the reaction is that at which the alloy of solvent metal and magnesium melts. This is around 800° C. for a silver-magnesium alloy. The melting temperature of the alloy chosen can be easily determined by melting a small piece of alloy in a vacuum, and the temperature of formation of the magnesium oxide film is then held sufficiently below this point so as to avoid damage.

Therefore, one may initiate and conduct the reaction for forming the magnesium oxide film at any temperature in the range of, say 400° C. up to slightly less than the melting point of the magnesium containing alloy.

The time for the reaction is determined by the temperature. The higher the temperature, the quicker the magnesium oxide film is formed.

Hence, after the structure has cooled after the first baking, or even without cooling, the film formation can be initiated. For this purpose carbon dioxide which is substantially free from oxygen and water vapor is admitted into the evacuated system. I prefer to introduce CO_2 until a pressure of from 400 to 500 microns of mercury is established in the tube, but a greater or lesser amount can be used, as this is not critical. Thus carbon dioxide is preferably introduced until a pressure of about 450 microns of mercury is established. I prefer to then increase the temperature of the alloy structure to an amount sufficient, considering the time at which the temperature is held, to form the magnesium oxide film on the alloy within a reasonably short period. For example, the temperature may be raised to about 735° C. to 775° C. and not substantially exceeding 800° C. A temperature of 750° C. gives good results. Heating is accomplished by induction heating, and held at the selected temperature for a period sufficient to oxidize the magnesium at the surface of the alloy. This time may be calculated thermodynamically, or determined by trial. For example, about 1½ to 3 minutes is required for film formation at a temperature of 750° C. A time period of two minutes at 750° C. gives good results. During this period the magnesium oxide film is formed on the surface of the magnesium alloy.

I have discovered that the oxidizing of the surfaces in a tube of this character with air or oxygen containing gases is generally not feasible since the supporting structure, usually of nickel, is also oxidized and because gases such as oxygen and water are extremely injurious to oxide-coated cathodes (primary emitters), which may otherwise be present in the tube structure. The carbon dioxide used in my process is therefore substantially free from oxygen and water vapor. I have found that on a thermodynamic basis magnesium will readily oxidize in the temperature ranges stated in a carbon dioxide atmosphere and that a small amount of carbon monoxide is thereby evolved. The evolved carbon monoxide is not a disadvantage as it acts as a reducing agent in respect to nickel which is usually present as structural supporting elements of the tube. Accordingly, the magnesium becomes oxidized by the carbon dioxide present in the system at the temperatures aforestated and the carbon dioxide is reduced to carbon monoxide which is then present in very small amounts. This carbon monoxide in turn, at the temperatures stated, has the effect of reducing any oxides of nickel that may be present on the nickel supporting structures within the tube assembly. In addition neither the carbon monoxide nor carbon dioxide present is injurious to oxide-coated cathodes (primary emitters), which may otherwise be included within the assembly.

In order to insure this protective action of the carbon monoxide in respect to the nickel components, the carbon monoxide must be present at a partial pressure which is in turn determined by the conditions of carbon dioxide pressure and temperature chosen for the formation of the magnesium oxide film. Thus, when operating at 750° C. the ratio of the partial pressures of CO_2 to CO is preferably 275–325 to 1. For other operating temperatures, this ratio may be calculated according to known thermodynamic methods. Too much carbon monoxide present will lead to deposition of carbon, which is a disadvantage. I prefer therefore to introduce a slight proportion of CO along with the CO_2 so as to insure the desired protective action at the outset of and continuously throughout the reaction, when nickel is present in the mechanical structure of the tube, as is almost always the case in modern vacuum tube construction.

After the magnesium oxide film has been thus produced upon the magnesium alloy secondary emission surfaces within the tube, the system is given another bake-out in a high vacuum and at temperature gradually elevated to 450° C. as previously described, to drive off absorbed gases, and the tube is then finally sealed and is ready for use.

It is apparent that many modifications and variations of this invention as hereinbefore set forth may be made without departing from the spirit and scope thereof. The specific embodiments described are given by way of example only and the invention is limited only by the terms of the appended claims.

What I claim is:

1. The method of preparing secondary emitter surfaces for electron tubes comprising forming the surface of a cleaned shape composed of an alloy of magnesium and a metal which is lower on the electromotive scale than nickel and in which magnesium is sufficiently soluble to form an alloy, mounting said shape and associated electron tube components on a supporting structure, sealing the said mounted shape and components in a gas impervious envelope, heating and simultaneously evacuating said envelope until it is out-gassed, then admitting into said envelope a fraction of an atmosphere of carbon dioxide containing a minor percentage of carbon monoxide, the temperature of the enclosed shape being maintained for a time sufficient to oxidize the magnesium on the surface of said alloy shape to magnesium oxide, thereafter heating an evacuating said envelope until it is finally out-gassed.

2. The method of claim 1 further characterized in that the enclosed shape is maintained at a temperature below the melting point of said alloy but not substantially lower than 400° C. until magnesium oxide is formed on the surface of said enclosed shape.

3. The method of claim 1 further characterized in that the enclosed shape is of silver-magnesium alloy and is maintained at a temperature below the melting point of said alloy but not substantially less than 400° C. until magnesium oxide is formed on the surface of said shape.

4. The method of claim 1 further characterized in that the enclosed shape is silver-magnesium alloy and is maintained at a temperature in the range of 725° C. to 775° C. for a period of 1½ to 3 minutes.

5. The method of claim 1 further characterized in that the envelope and components are out-gassed by heating to a temperature in the range of from 400° C. to 500° C. while simultaneously evacuating the envelope to a pressure of around 1×10^{-6} mm. Hg, said heating being gradually increased so that said pressure does not exceed 1×10^{-4} mm. Hg pressure.

6. The method of claim 1 further characterized in that the carbon dioxide containing a minor percentage of carbon monoxide which is introduced is introduced in amounts to provide an atmosphere of from 300 to 500

microns of Hg pressure and the enclosed shape therein is heated by induction heating to about a temperature not substantially exceeding 800° C. until said magnesium oxide film is formed.

7. The method of claim 6 further characterized in that the heating is for not more than three minutes.

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