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METHODS OF PROCESSING SILVER-MAGNESIUM SECONDARY EMITTERS FOR ELECTRON TUBES

RADIO CORPORATION OF AMERICA
RCA LABORATORIES DIVISION
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Introduction

A silver-magnesium alloy (with the order of a per cent of magnesium in silver) is widely used in experimental electron tubes as a good secondary-emitting surface. Best results require a processing procedure which leads to a thin, straw-colored, magnesium-oxide surface. At the start of the present work, it was believed that such a surface could be prepared by baking the cleaned and polished alloy in oxygen or water vapor or both. It was found, however, that dry oxygen would not form the desired surface, whereas presence of water vapor did produce good secondary emitters. Subsequent experiments showed that, because of the rapid diffusion of oxygen through heated silver, the magnesium in the alloy was oxidized in situ without diffusing to the surface to form a layer. With water vapor as an oxidizing medium, the diffusion rate of magnesium through the silver greatly exceeded that of the water vapor, and a satisfactory surface layer was formed. A technique was then devised in which an original water vapor process formed the desired surface, followed by an oxygen process to oxidize the remanent magnesium throughout the volume of the alloy. With this technique, good secondary emitters are possible which will withstand severe overheating without the evaporation of magnesium found with earlier techniques.

General Discussion

The best-known secondary-electron emitters are those that consist of an oxide film on a metal electrode base. For example, such an emitter is obtained when an alloy of 98.3 per cent silver and 1.7 per cent magnesium[1] is baked for a suitable time in an oxidizing atmosphere. Fig. 1 shows a drawing indicating schematically the structure associated with an activated emitter of this kind. The surface film has been identified as magnesium oxide by electron diffraction studies and its thickness measured to be about 1250 Angstrom units.[2] Properly prepared silver-magnesium (AgMg) alloy surfaces have the following excellent characteristics for use in vacuum tubes:

1. High secondary emission ratios that remain constant for several thousand hours.
2. Low surface and interface resistances, so that arcing and Malter effect[3] do not occur, thus giving good high-frequency performance.
3. Ease and uniformity of activation of the alloy once the proper parameters are set.
4. No deterioration of the activated sample upon a few hours' exposure to air.
5. No further activating required after the emitter is placed in the vacuum tube.

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[1] V. K. Zworykin, J. E. Ruedy, and E. W. Pike, "Silver Magnesium Alloy as a Secondary Electron Emitting Material", *Jour. App. Phys.*, Vol. 12, pp. 696-698, September 1941.

[2] P. Rappaport, "Optical Thickness Measurements of MgO on AgMg Secondary Emitters", MIT Eleventh Annual Conference on Physical Electronics Report, pp. 70-73, March 1951.

[3] L. Malter, "Thin Film Field Emission", *Phys. Rev.*, Vol. 50, pp. 48-58, July 1936.

Two difficulties connected with this type of emitter are its inability to withstand heat because of evaporation of the magnesium remaining in the alloy, and the poor secondary-emission ratios that many workers experience because of incorrect application of the processing technique.

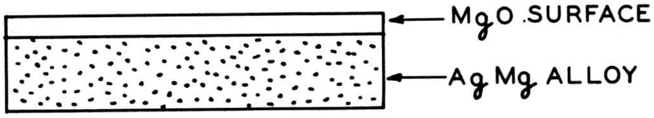

Fig. 1 - Silver magnesium secondary emitting surface showing thin MgO film.

The work described in this bulletin leads to a better understanding of the oxide-film formation on the silver-magnesium alloy. It is believed that at elevated temperatures the magnesium becomes mobile in the silver and some of it may diffuse to the surface of the alloy. There it will either evaporate or combine chemically and thus create a diffusion gradient to the surface for magnesium ions. Since magnesium oxide is the desired product on the surface of the alloy, it is necessary to expose the heated alloy to oxygen. However, pure uncombined oxygen diffuses so readily through hot silver that internal rather than surface oxidation results. On the other hand, use of other oxidizing media, such as water vapor, gives satisfactory oxide films on the surface. The experiments which led to these conclusions are described below and a new combination process for a superior secondary emitter is outlined.

Method of Attack

An empirical approach to the problem was undertaken. Processing experiments were performed by baking the alloy surface in various atmospheres for various times and temperatures, with separate control of the important parameters. The atmospheres used included oxygen, air, nitrogen, helium, hydrogen, and water vapor. The pressure was varied from atmospheric to 10^{-8} mm Hg. Time of heating varied from a few minutes to four hours and the temperature from about 400 to 700 degrees C.

Great care was taken in the experiments to eliminate equivocal results wherever possible. Baking was almost always done in a quartz tube which was evacuated by an ordinary mechanical pump and a mercury diffusion pump. When necessary, the gases introduced into the processing system were dried through cascaded liquid air traps and, for purity of certain gases, clean charcoal traps at liquid air temperatures were employed. It was sometimes necessary to flush out the system a number of times to insure purity of the baking atmosphere. Special polishing and cleaning techniques for the alloy were employed, as follows. After polishing on a standard clean cloth buffing wheel, the sample was washed in a soapy water solution, then rinsed in distilled water, followed by a distilled acetone and methanol mixture.

The results of the various processes were evaluated by the physical and electrical properties of the treated samples. Appearance, mechanical flexibility, electron and x-ray diffraction, evaporation of heated samples, secondary-emission ratio and life tests in electron tubes all gave important clues. A test was developed in which a drop of mercury was applied to the surface of a processed sample and then withdrawn. By noting the difference in wetting action, an oxidized surface can be differentiated from an unoxidized one. For example, if an unprocessed sample of silver magnesium alloy is contacted by the mercury drop for even a very short time, some of the mercury will stick to it, while an oxidized sample remains free from any mercury even though there is contact for quite a long time.

Experimental Results

Table I lists the important characteristics of a series of AgMg samples after they were baked in different atmospheres. The treatments of the alloy are listed in the vertical column of the table. The standard processing technique, referred to as Process No. 1, had been believed to be the most reliable and reproducible method for the processing of AgMg into good secondary emitters and was developed after many years of work at RCA Laboratories. This technique consists essentially of baking the clean alloy at 550 degrees C for ½ hour in a quartz oven to

Table I

CHARACTERISTICS OF AgMg ALLOY (1.7% Mg) SAMPLES WHEN PROCESSED BY VARIOUS METHODS

Process No.	Baking Atmosphere *	Water Vapor Pressure mm Hg	Secondary Emission Ratio	Appearance	Presence of Oxide Film (Mercury Test)	Flexibility	Magnesium Evaporation	Further Oxidation Possibilities
1	Vacuum (Standard process)	5×10^{-4}	Good	Shiny Yellow Film	Yes	Yes	Much	Yes
2	Vacuum (Liq. air trap)	$<10^{-8}$	Poor	Metallic	No	Yes	Much	Yes
3	Air 760 mm Hg	No Drying	Poor	Patchy Dull White Film	No	(Very Brittle) No	Very Little	No
4	Air 10^{-2} mm Hg	No Drying	Poor	Patchy Dull White Film	No	(Less Brittle) No	Little	No
5	Oxygen 760 mm Hg	$<10^{-8}$	Poor	Patchy Dull White Film	No	(Very Brittle) No	Very Little	No
6	Helium Wet	No Drying	Good	Shiny Yellow Film	Yes	Yes	Much	Yes
7	Helium Dry	$<10^{-8}$	Poor	Metallic	No	Yes	Much	Yes
8	Nitrogen	No Drying	Not Tested	Patchy Dull White Film	No	?	?	?
9	"Dry" Hydrogen	8×10^{-3}	Good	Shiny Yellow Film	Yes	Yes	Much	Yes
10	Two-Step Process		Good	Shiny Yellow Film	Yes	(Brittle) No	Very Little	No

*Baking done at 550 degrees C for ½ hour for all processes except 9 and 10.

which water vapor has been added and then pumping out to about 10^{-5} mm Hg using a dry ice and acetone cold trap. The characteristics of such a sample, listed in the table, are all good except for the fact that magnesium evaporates out when the sample is heated.

The treatments from Process No. 1 to No. 6 were all in the same chamber and with baking for ½ hour at 550 degrees C. Water vapor was added intentionally only in Process No. 1. In Process No. 2, a liquid air trap was used and the system pumped down to about 10^{-6} mm Hg before baking. No detectable change of the alloy took place except for a general outgassing and cleaning. In Process No. 3, the sample was baked in air with no drying, and in Process No. 4 the system was pumped down to 10 microns before baking took place. Process No. 5 took place in pure dry oxygen at atmospheric pressure. In Process No. 6 the chamber

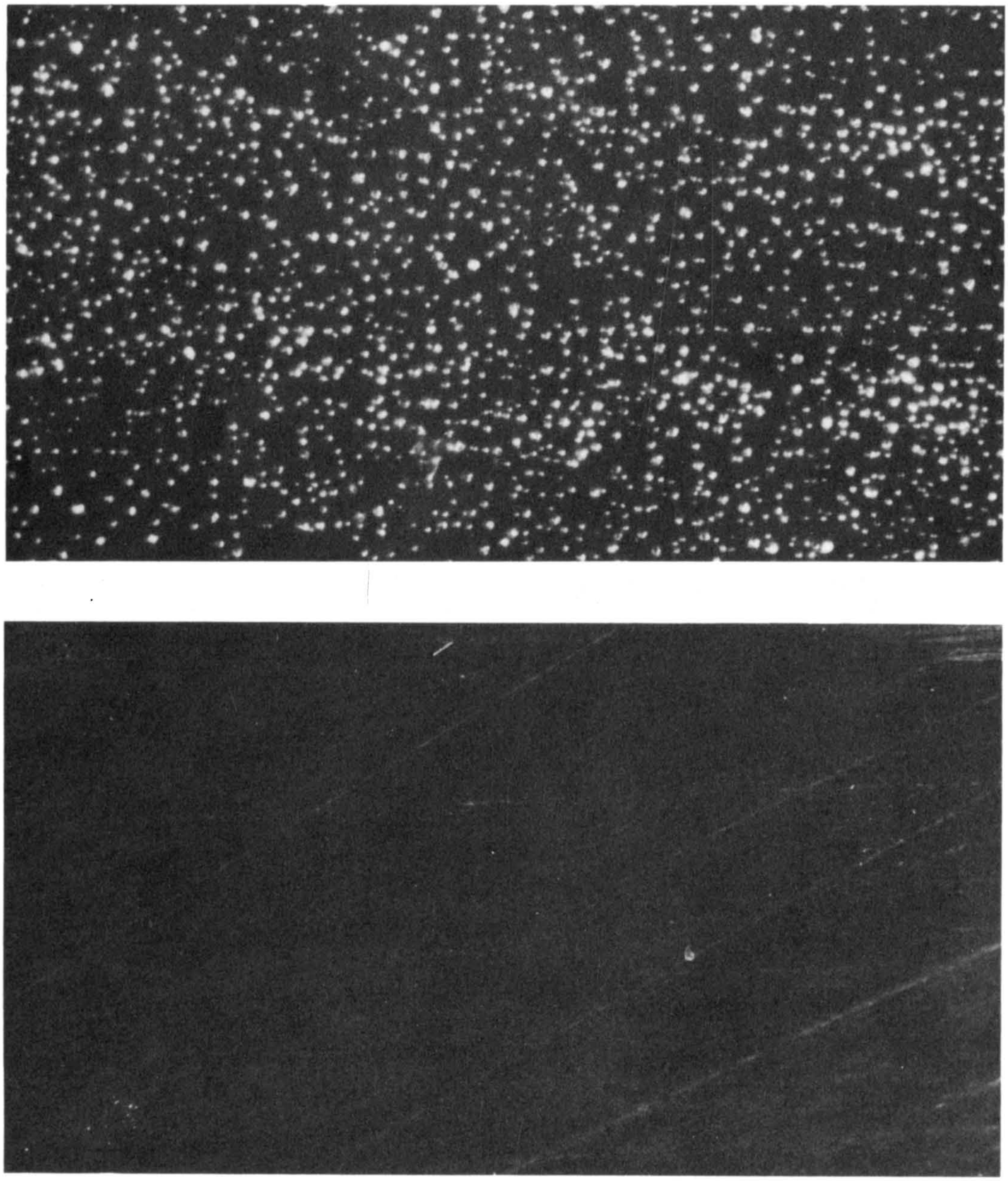

Fig. 2 - Micro-photographs (magnified 200 times) of processed AgMg surfaces. Top-sample baked in oxygen as in Process No's 3, 4 and 5. Below - sample processed in water vapor as in Process No. 1.

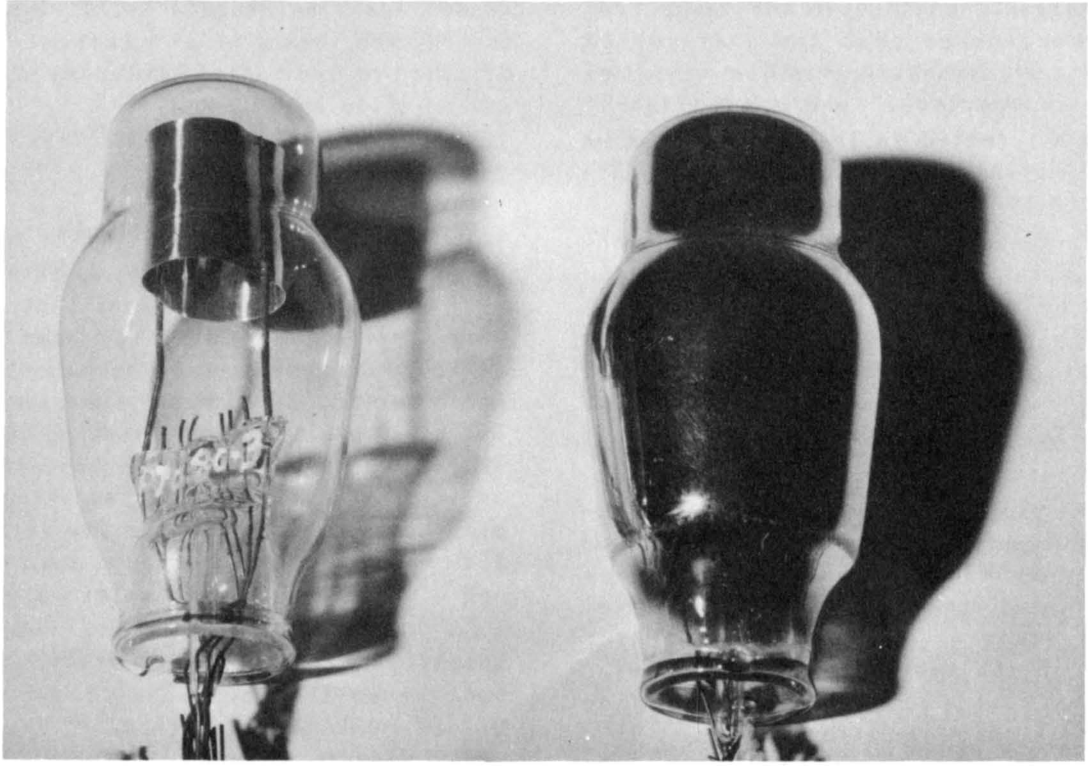

Fig. 3 - Appearance of vacuum bulbs after samples contained have been "RF" heated to 775 degrees C. Tube on right contains a normally processed AgMg emitter. Tube on left contains a two-step processed emitter.

was filled with helium directly from a tank with no drying precautions, whereas in Process No. 7 charcoal in liquid air traps was used and the system was flushed out three times before baking. Nitrogen directly from a tank was used in Process No. 8 and in No. 9 a sample was baked in a so-called "dry" hydrogen furnace for 5 to 10 minutes.

If a sample was processed as in No. 10 of the table, which is Process No. 1 followed by Process No. 5, it became brittle but had a good ratio as shown in the table. This so-called two-step process will be discussed later in another connection.

The top row of the table lists the characteristics of the processed alloy. The photograph in Fig. 2 shows the typical appearance of processed samples. The upper one shows what is meant by patchy, and the lower one is the shiny yellow referred to in the table. These are microphotographs magnified about 200 times. Polish lines are visible on both samples. The shiny yellow oxide film on the lower photograph is transparent so that the underlying alloy is visible. The white spots on the upper photograph are probably dots of MgO appearing to the unaided eye as a milky white film on the surface of the alloy. The dark regions are probably silver, as indicated by the mercury drop test. The drop immediately wet the surface which must mean that some silver base metal had been exposed at the surface. Tests with H_2S verified these results. The silver regions blackened due to the formation of silver sulfide. Comparisons with crystal grain boundaries did not show any correlation with the white dots. The dots were much more numerous and more evenly spaced than the grain boundaries.

The test for flexibility is important because it gives information concerning the internal structure and composition of the sample. In the table, "yes" means that the flexibility is the same as that of the original AgMg alloy which was quite flexible. When the samples became brittle, they were incapable of any flexing, breaking much the same as a razor blade would.

A secondary-emission ratio of 3.5 or over in the table is considered good. A ratio of 1.2 is the approximate value observed for unprocessed AgMg alloy. Readings in the range from 1 to 2 are considered poor for a processed surface. Tests of secondary emission were made in rotating dynode tubes[4] where a number of surfaces are all tested in the same bulb so as to eliminate variations due to different tube processing.

Tests for magnesium evaporation were conducted on samples placed in vacuum bulbs and then heated by radio frequency to about 775 degrees C. The amount of evaporation was estimated qualitatively by the light transmission of the metallic film appearing on the inside bulb wall. Fig. 3 shows two bulbs tested in this manner.

The ease with which a sample may be reprocessed, (i.e., further formation of an oxide film on a sample that has had previous processing) indicates something about the physical and chemical state of the processed sample. As indicated in the last column of the table, after Process No. 1, a sample can be made darker by additional oxidation. However, this can be done only within narrow limits. Of course, after Process No. 2, vacuum baking, the sample can be oxidized. The interesting thing is that after Processes No. 3, 4, 5, 8 and 10, no further oxidation is possible.

Note that the characteristics of samples treated as in Processes No. 1, 6, and 9 are very similar. A processed sample can be made almost identical by any one of the three processes if the conditions are properly controlled.

Some further important experiments were performed. When a sample of AgMg alloy was coated with a thin goid film by evaporation and then baked in oxygen, as in Process No. 5, it remained flexible and had an oxide surface. This was remarkably different from the non-gold coated sample of AgMg. Further processing was possible by Process 1 but the sample was not tested for secondary emission.

When a sample of AgMg alloy was coated with silver about 1000 Angstrom units thick, it was still possible to form a magnesium oxide on its surface by Processes No. 1, 6, or 9. Further, if the once-processed oxidized sample was again coated with a silver film and processed again by Process No. 1, a second oxide coating was formed which had the characteristic of Line 1 of the table (including a good secondary emission ratio).

Discussion of Results

The striking conclusions that can be drawn from these experiments are: When samples are baked in oxygen-containing atmospheres as in Processes No. 3, 4, and 5, very poor secondary emitters result, but when baking in atmosphere where oxygen is not present and water vapor is, as in treatments No. 1, 6, and 9, good emitters are obtained. This is opposite to the expectation that pure oxygen should form the MgO film and give good secondary emitters.

The following qualitative picture is supported by the experimental results. It is well known that oxygen diffuses through hot silver in large quantities.[5,6] The addition of small amounts of magnesium does not appear to affect this phenomenon very much. Magnesium diffuses through the hot silver readily but not nearly so fast as the oxygen. Magnesium oxid and water vapor molecules hardly diffuse through silver at all because of their large size. The present experiments have shown that oxygen and magnesium also diffuse through the thin MgO surface when formed on the alloy. When the AgMg alloy is baked in an oxygen atmosphere, the oxygen diffuses into the alloy much faster than the Mg can diffuse to the surface. As the oxygen penetrates the alloy, it combines with any magnesium atoms that it contacts; the MgO formed is immobile and is frozen in place, thus preventing any formation of a surface MgO film, except where Mg atoms are on or near the surface, about 1 out of every 13 atoms.

The brittleness formed in the alloy prepared with oxygen is due to the effect of the internally formed MgO on the silver lattice. The patchy appearance of the surface, the mercury drop test and the secondary-emissio tests all confirm that a continuous MgO fil

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[4] C. W. Mueller, "Receiving Tubes Employing Secondary Electron Emitting Surfaces Exposed to the Evaporation from Oxide Cathodes", *Proc. I.R.E.*, Vol. 38, pp. 159-164, February 1950.

[5] E. W. R. Steacie and F. M. Johnson, "Solubility and Rate of Solution of Oxygen in Silver", *Proc. Roy. Soc.*, Sec. A, Vol. 112, p. 542, 1926.

[6] F. M. Johnson and P. Larose, "The Diffusion of Oxygen Through Silver", *Jour. A.C.S.*, Vol. 46, pp. 1377-1389, 1924.

did not form on the surface. Finally, since it was not possible to oxidize further the sample or evaporate any magnesium from it, it is concluded that substantially all of the magnesium in the sample had been oxidized without producing a good secondary-emitting surface layer.

When the alloy is baked in an oxygen-free atmosphere with some other oxidizer such as water vapor, which does not readily diffuse into the alloy, the picture is different. In this case, the magnesium is allowed to diffuse to the surface before it is oxidized by the action of water vapor and heat, and a good secondary-emitting layer is formed. That free magnesium is present inside such a sample is evident from the high evaporation rate when a water-vapor processed sample is heated and also from its ability to form further oxides on top of evaporated silver films. Water-vapor processed samples are mechanically as flexible as the original AgMg alloy. The results in Table I demonstrate the effect of water vapor in the processing atmosphere. The interesting point about the "dry" hydrogen process is that free oxygen cannot exist and can definitely be eliminated as a contributor to the oxide film formation.

The results with the gold-covered AgMg sample which did not become brittle and was capable of reprocessing after baking in oxygen can now be explained. Since the oxygen diffuses through gold slightly, compared to silver, none of the internal free magnesium was oxidized. The magnesium now diffuses through the gold film and becomes oxidized on the surface.

The Improved Processing Technique (Process No. 10)

Since water vapor cannot penetrate the alloy when it is used as the oxidizing agent, any magnesium that has not arrived at the surface is still present in the metallic form, inside the volume of the alloy. This magnesium can evaporate out if the emitter is overheated, as is readily possible during processing or operation of electron tubes. This is highly undesirable because the evaporation of magnesium may cause leakage and r-f losses.

An extension of the above techniques can cure this undesirable property. The experiments here described have shown that, when a water-vapor processed AgMg sample is subsequently heated in oxygen, it becomes brittle and evaporation of magnesium after overheating is almost completely eliminated. The effect indicates that oxygen penetrates the already formed MgO film and oxidizes the remaining free magnesium atoms in the alloy, thus freezing them in place. Fig. 4 shows a simplified illustration of such an emitter after the two-step activation process.

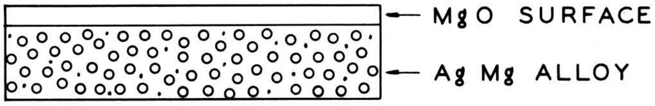

Fig. 4 - Silver magnesium secondary emitting surface after the two-step processing. The circles represent MgO molecules and the dots represent remaining magnesium atoms.

Measurements in a vacuum were made to determine the amount of magnesium evaporation at 775 degrees C from the two-step-activated sample by comparison with evaporation from samples of AgMg with known Mg concentration. The results show that when a water-vapor activated sample was subsequently baked at 700 degrees C in oxygen at atmospheric pressure for 5 minutes, the magnesium evaporation in a vacuum was about one-twentieth that of a similar sample without oxygen bake. Fig. 3 shows two bulbs containing geometrically-similar samples that were heated to 775 degrees C. The bulb on the right contained a normally processed sample (water-vapor only) and the one on the left the two-step-activated sample (water vapor followed by oxygen). Even in the photograph, the difference in evaporation is striking. Fig. 5

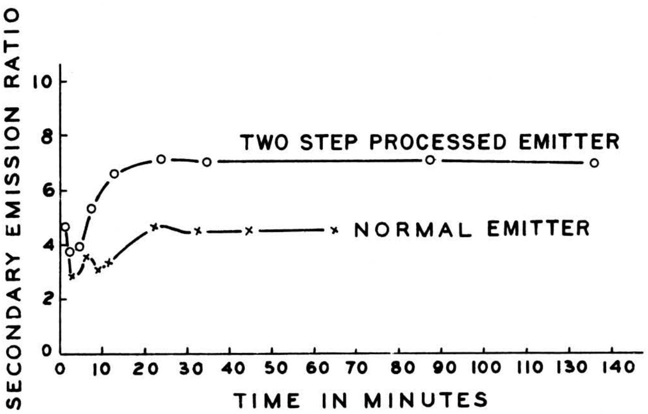

Fig. 5 - Secondary emission test at 300 volts showing effect of two-step processing of AgMg alloy. Emitters in same bulb on demountable system.

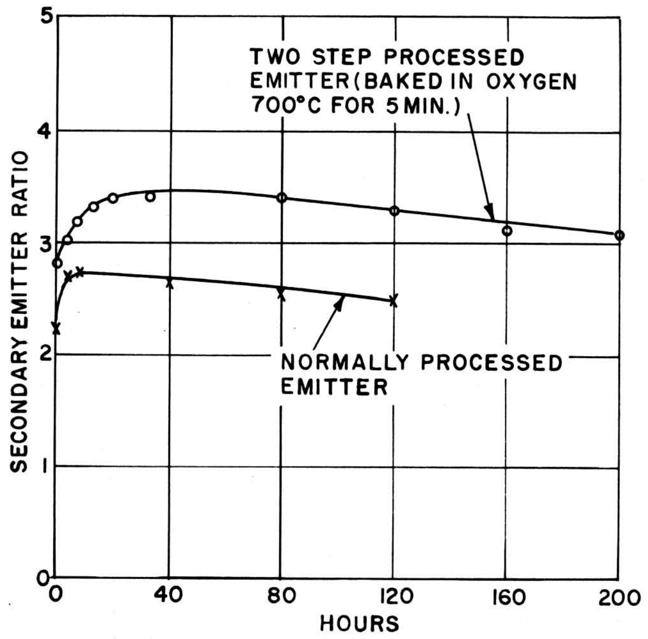

Fig. 6 - Comparison of life tests of AgMg secondary emitters in same sealed-off and gettered bulb.

shows the secondary emission ratio of the two-step activated sample in comparison with the one-step activation both in the same demountable bulb. A significant increase in ratio was observed by this treatment probably because of the effect of the oxygen in the MgO surface. Some free Mg in the surface may have been oxidized which would have increased the mean free path for secondary electrons and given rise to the greater yield. Fig. 6 shows comparisons o 200-hour life tests in the same sealed-of bulb. It should be noted that the ratios in Fig. 6 are lower than those in Fig. 5. This is often observed when comparing results between demountable and sealed-off tubes. The surfaces are apparently sensitive to small variations in tube atmosphere.

Conclusions

A description has been presented of what takes place when silver-magnesium alloy is processed for making secondary emitters. In general, oxygen has been shown to be detrimental to the initial purpose of building an MgO film on the alloy because of its great solubility in hot silver. Water vapor, because of its oxidizing ability and its inability to diffuse into the alloy, has given successful, reproducible, long life, and high ratio secondary emitters. Further application of the principles has resulted in a two-step activation process which gives an even higher ratio secondar emitter whose tolerance, with respect to overheating, is far superior to existing AgMg secondary emitting surfaces.

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