Tungsten, Thoriated-Tungsten, and Thoria Emitters

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PURE-TUNGSTEN EMITTERS

Tungsten has been used for many years as the source of electrons in high-power tubes. Until relatively recently, all tubes operating at plate voltages above 5000 volts used pure-tungsten emitters because of their resistance to high-energy gas ions, which attack oxide-coated and thoriated-tungsten cathodes.

Although tungsten has the relatively high work function of 4.56 volts, its high melting point (3655 K) and great mechanical strength make it possible to operate cathodes at temperatures high enough to achieve practical emission levels.

Preparation of Tungsten Filaments

Ductile tungsten was first produced by Coolidge in 1909. Because of its high melting point, powdered-metallurgy techniques were employed and are still in use today. Tungsten powders are compressed into bars under pressures of about 30 tons per square inch at room temperature, and the bars are then presintered in a furnace at about 1250 C. These bars, which are porous and weak but sufficiently strong to be handled, are then sintered by passage of several thousand amperes through them to heat the tungsten almost to its melting point. During this process the metal powder sinters and the volume shrinks about 17 per cent. The tungsten bar is then very strong, but quite brittle. In the next step, it is hot-swaged down to a small rod size by rotating hammers. Swaging produces an elongated crystal structure which makes the metal ductile.

The tungsten is then ready for drawing or rolling to produce the wire sizes used in filamentary cathodes, The tensile strength of wire produced in this manner may reach 500,000 pounds per square inch; such wire is reasonably ductile. Required "bends" can be made cold, but severe working is best accomplished at temperatures between 800 and 1000 C. The long fibrous structure of pure (undoped) tungsten remains until the wire is heated above 1200 C. At this temperature the metal begins to recrystallize into a fine-grain structure and suffers a loss of ductility. At the high temperatures (2400 K) required for electron emission, the grains continue to grow and eventually form large crystals which cause the filaments to become extremely fragile. In some instances the crystals may extend completely across the diameter of a filament, and the resulting offsetting may cause the filament to break mechanically long before failure due to normal evaporation occurs. Efforts to produce single-crystal wire and "doped" wire to prevent grain growth and offsetting have been moderately successful. Thoria was used as an early addition to pure tungsten to inhibit grain growth; the fact that it also greatly enhanced the electron-emission properties of tungsten proved to be an unexpected extra dividend.

The grain size of tungsten is of considerable importance when the wire is severely worked. When round wire is rolled into strands having odd-shaped cross-sectional configurations, wire having 1000 grains per square millimeter, since it works more easily than coarser-grained material, is far better for achieving uniform dimensions. However, fine-grain tungsten has low creep strength so that, for maximum life, tungsten having large grain structure (less than 500 grains per square millimeter) is desirable. Grains should have a length-to-width ratio of at least 5 to 1 to achieve high strength. Because the grain size is controlled by the tungsten supplier, close cooperation between the maker and the user of tungsten is very desirable for achieving a proper balance between workability and strength.

Properties of Tungsten Emitters

Electrons are emitted from tungsten when sufficient thermal energy is induced to cause the electron to cross the surface-boundary region. The properties of tungsten, its emission characteristics, and the emission properites of various materials have been thoroughly studied and are well covered in the literature[1-20].

Emission from pure metals such as tungsten follows the Richardson-Dushman equation as closely as can be determined experimentally. This relationship is:

$$I_S = AT^2 \epsilon^{-b_o/T} \qquad (1)$$

where I_S = Emission current — amperes
A = Constant for the emitting material — amperes/square centimeter/deg K
T = Absolute temperature — deg K
b_o = Constant corresponding to the temperature required for all of the free electrons in the material to be emitted — deg K

Table I shows the values of A, work function ϕ, and b_o for several pure-metal emitters; thoriated tungsten is included for comparison.

TABLE I

Emission Factors for Tungsten and Some Other Metals

Emitter	A amp/cm^2/deg^2	Work Function ϕ Volts	b_o degrees K
W	60-100	4.54	52,400
Ta	60	4.1	47,200
Mo	60	4.15	51,300
Th on W	3.0	2.63	30,500

The thermionic properties of tungsten are well known; Table II shows some of these properties which are important to tube designers.[21] In this table, there are certain important properties to be noted. First, it is apparent that there is a large increase in resistance with temperature. This increase must be accommodated by heating the tungsten filament slowly to prevent burnouts caused by sudden surges of current. (This precaution also applies to thoriated tungsten, although to a lesser degree.) Second, the power radiated is so high at practical emission levels that this type of filament is basically inefficient. At a given emission level, pure tungsten requires about six times as much heating power as thoriated tungsten, and about 30 times as much as oxide-coated cathodes.

Table II also shows that the emission level is a steeply rising function of temperature; however, the evaporation-rate rise, shown in the last column, is even steeper. The evaporation rate becomes a critical factor as the operating temperature increases.

Filament life is assumed to end when 10 per cent of the metal has evaporated, because hot spots and burnouts usually occur at this point. Tubes having filaments of less than 0.010-inch diameter are generally operated at approximately 2400 K. Tubes having filaments of larger diameter can be successfully operated up to 2800 K because the percentage loss due to evaporation becomes smaller with increasing bulk of the emitters.

Oxygen increases the work function of tungsten to 9.2. Other electronegative elements also reduce the emission capabilities of tungsten. For this reason, tungsten emitters must be clean to achieve design-emission levels. A tungsten filament is usually cleaned by heating it to somewhat above its operating temperature for approximately 30 minutes to degas the material throughout. A final flash at 3000 K for approximately one minute removes all the surface oxide and provides a clean emitting surface. This treatment is usually given to the filaments during exhaust and processing of the assembled tubes.

Present Uses

Recent work[22, 23] has shown that the more efficient thoriated-tungsten filament can be used at high voltages and in high-power tubes; new tubes, therefore, are no longer being designed with pure-tungsten emitters. However, several tubes using pure-tungsten emitters, such as the 207, 891, 892, 880, 9C21, and 9C22 are still in production. Pure-tungsten emitters are also used in tubes, such as continuously pumped Resnatrons for particle accelerators, where the degree of vacuum is too poor for thoriated-tungsten operation.

THORIATED-TUNGSTEN EMITTERS

Langmuir[24] discovered that thoria (thorium oxide), previously mixed with tungsten to reduce grain growth in tungsten filaments, could greatly increase thermionic emission under proper conditions. It was found that metallic thorium, produced by reduction at high temperatures, diffused to the surface of the tungsten to produce a layer one-molecule thick. It was further found that the electropositive dipole effect of this monomolecular layer reduced the work function of the tungsten to 2.63, which is less than the value of 3.35 for pure thorium.

Preparation

Thorium oxide is added to the tungsten powder in proportions between 0.7 and 2 per cent. The finished thor-

TABLE II

Thermionic Properties of Tungsten at Various Temperatures

Temperature deg K	Resistivity microhms/cm	Total Radiation Intensity watts/ cm^2	Electron Emission amp/cm^2	Rate of Vaporization grams/cm^2/sec
300	5.64	0.0015	--	--
600	13.54	0.048	--	--
900	22.58	0.379	--	--
1200	37.02	1.691	--	--
1400	38.52	3.82	5.75×10^{-9}	--
1600	45.22	7.77	8.05×10^{-9}	3.7×10^{-20}
1800	52.08	14.22	3.92×10^{-5}	6.22×10^{-17}
2000	59.10	23.72	8.92×10^{-4}	2.32×10^{-14}
2200	66.25	37.18	1.14×10^{-2}	2.90×10^{-12}
2400	73.55	55.8	1.02×10^{-1}	1.58×10^{-10}
2600	81.0	80.8	6.48×10^{-1}	4.64×10^{-9}
2800	88.5	112.9	3.21	8.28×10^{-8}
3000	96.2	153.9	--	9.92×10^{-7}

iated filament must be flashed to a high temperature (2800 K) to reduce some of the thoria to thorium metal. At this temperature thorium diffuses to the surface and rapidly evaporates so that the emission at high temperature is essentially that of pure tungsten. If the temperature is then reduced to between 2000 and 2200 K, the rate of diffusion is still quite high, but the rate of evaporation is reduced to the point where a monomolecular layer can form on the surface. This treatment is known as activation and usually is accomplished in 15 to 30 minutes during tube processing. The filament temperature may then be reduced to the operating range of 1900 to 2050 K, where generous electron emission occurs and the rate of thorium evaporation is substantially equal to the rate of diffusion to the surface.

Thorium apparently diffuses to the surface along grain boundaries and spreads over the surface by migration. The surface coverage depends on the orientation of the tungsten crystals; certain faces show preferential adsorption. It is also believed that finer-grain material is beneficial because many more paths are available for outward diffusion of thorium and, therefore, coverage can be accomplished more quickly.

Reasons for Carburization

It has long been the practice to form a layer of tungsten carbide on the surface of thoriated-tungsten filaments. Tungsten carbide greatly reduces the rate of evaporation of thorium from the surface[25]; at 2200 K, for instance, the rate of evaporation is reduced 83 per cent. In addition, the fine grain structure produced by the preferred type of carbide assists rapid diffusion of thorium to the surface. Higher-temperature operation and greater thorium mobility make the carburized filament much more rugged in the presence of gas ions.

This rugged carbide layer, together with the better vacuums and cleaner parts of modern tubes, and the increased protection offered by "crowbar" circuits[26], have made it possible to use thoriated-tungsten filaments in tubes having plate voltages as high as 40,000 volts.

According to Ayer, the life of a carburized filament is essentially a function of carbide thickness, as shown in Fig. 1. More recent information indicates Ayer's curves to be conservative, although they are still highly useful in tube design.

The Carburization Process

The carbide layer is formed by heating the filament in a carboniferous atmosphere so that carbon reacts with the tungsten surface to form a shell of carbide around the filament. Past practice has been simply to carburize until a certain decrease in resistance of the filament showed that a certain percentage of the filament cross section was carburized. A 20-per-cent reduction in resistance was the average figure used.

It has been found most practical to carburize the filaments before they are inserted into tubes by heating them in a bell jar containing dry hydrogen and a hydrocarbon such as benzene or toluene. When the hydrocarbon vapor strikes the hot filament it dissociates, and at high temperature the carbon reacts with the tungsten to form tungsten carbide. A typical apparatus for performing this operation is shown in Fig. 2.

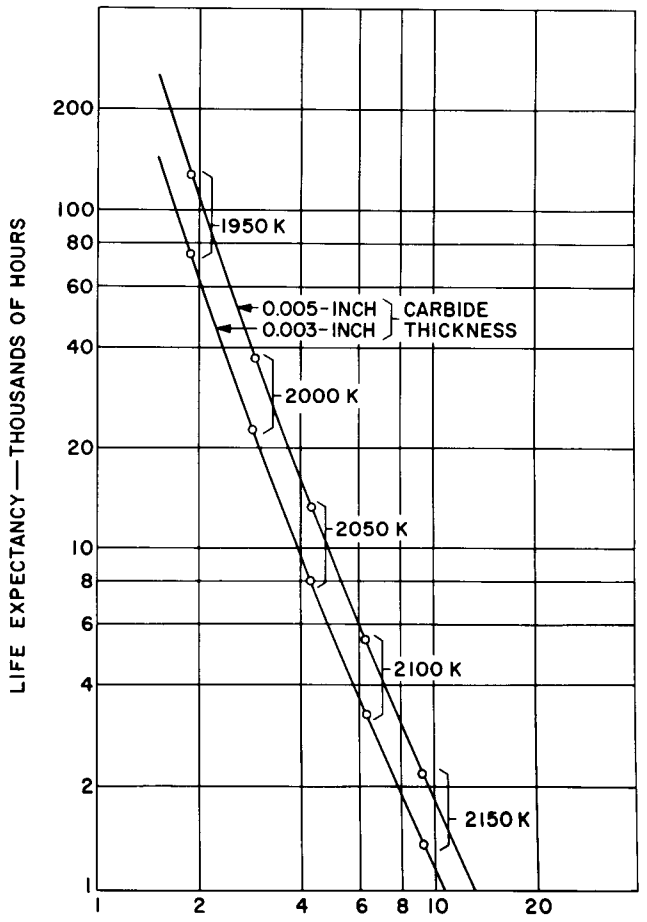


Figure 1. Life Expectancy and Emission for Thoriated-Tungsten Filaments for two Thicknesses of Carbide

Many carbides are possible in such a setup and, therefore, careful control of all parameters must be maintained to achieve the desired results. In 1947, Horsting[27] first showed that the carbon potential of the hydrogen atmosphere was important, not only for maintaining a uniform depth of carbide, but also for controlling the type of carbide. The various types of carbide possible for different carbon potentials when other conditions remain constant are shown in Fig. 3. There are many forms of tungsten carbide, all grouped around two chemical compounds, WC at 6.12 per cent carbon and W_2C at 3.16 per cent carbon, as shown in Fig. 3. The diagrams at the left of the figure illustrate a pie-shaped, cross-sectional area of a round wire. The figures at the right show the concentrations of carbon in tungsten in respective layers and their relative depth of penetration.

It can be seen that the stoichiometric WC produces a massive, unbroken carbide; W_2C is also a massive carbide but breaks up on radial lines. As the carbon concentration diminishes, a laminar carbide is formed in the region between 3.16 per cent C (W_2C) and 2.45 per

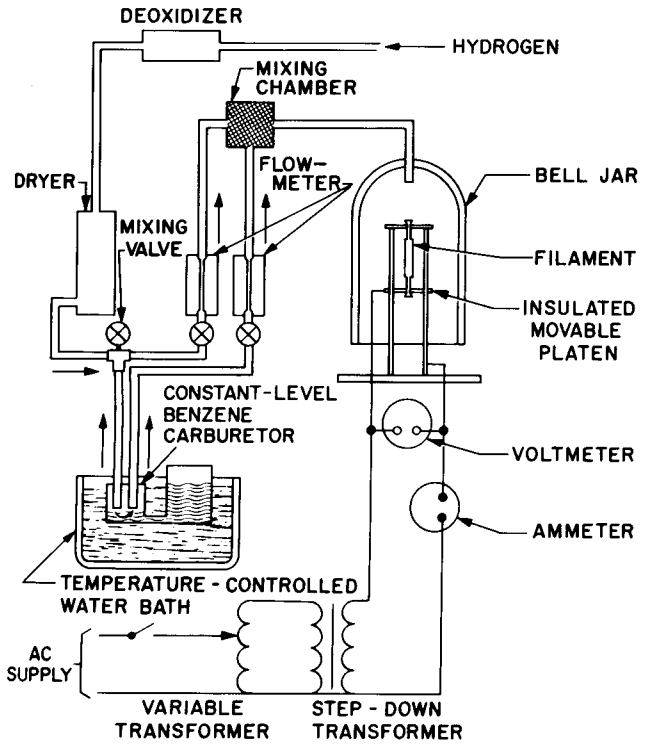


Figure 2. Typical Equipment for Carburizing Thoriated-Tungsten Filaments

cent C. This type of carbide is caused by a narrow region of solubility of tungsten in W_2C which precipitates out on cooling to form a laminated structure. Further reductions in carbon potential reduce the penetration but still maintain the laminar structure.

Further work[28] has indicated that the finely laminated structure, as shown in F of Fig. 3, is the desirable type for full, stable emission in high-power tubes. It is believed that the broken-up carbide structure allows the thorium to diffuse to the surface more readily and it is therefore available at all times for electron emission.

The typical cross section of a filament strand used in an RCA Super-Power tube in Fig. 4 shows the preferred type of laminar carbide. An example of the undesirable, massive type of carbide is also shown.

In most coiled filaments, the carbide is produced in a bell jar similar to that shown in Fig. 2. The filament is carburized to a specified per-cent change in resistance and is then mounted in the tube. The tube is then exhausted. During exhaust the filament is flashed and activated by the procedures mentioned previously. It has been found, in studies of this action, that a massive-type carbide is formed during carburization and is later reduced to the laminated phase by the flashing and activation processes. The carbon content of the carbide is reduced both by evaporation of carbon and by further penetration at these high temperatures. This method produces satisfactory filaments, but requires very close control of all parameters.

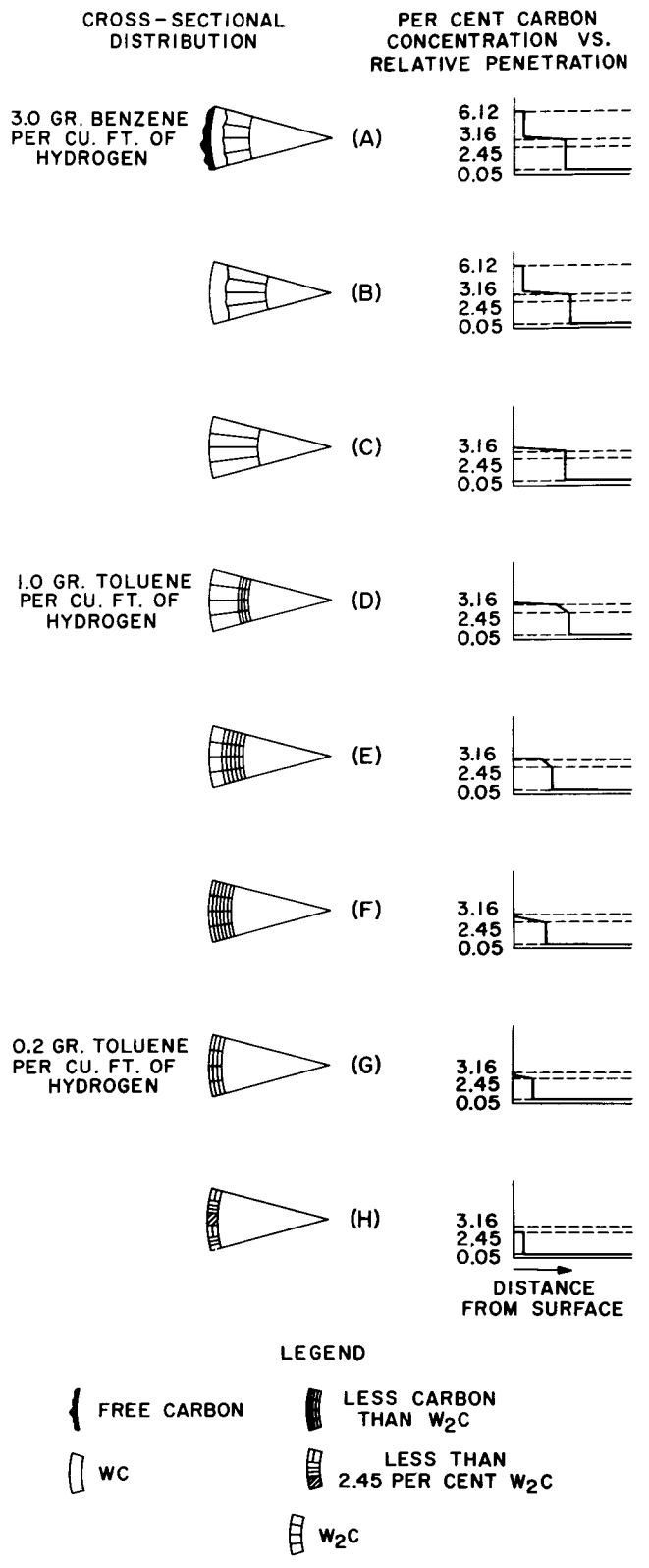
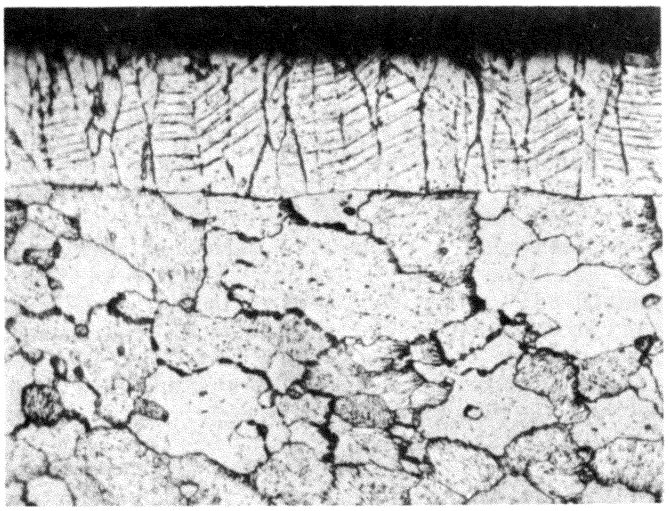


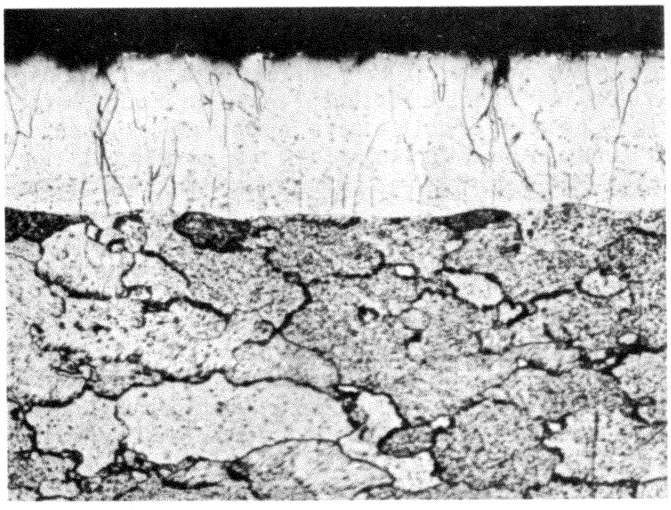
Figure 3. Distribution of Tungsten Carbides on Carburized Thoriated-Tungsten Wire

End-Loss Correction

In the design of straight-strand filaments for Super-Power tubes it was found that any system involving high-



(A)



(B)

Figure 4. Cross Sections of Carburized Thoriated-Tungsten Filaments: (A) preferred type of laminar carbide (272X); (B) undesirable massive type of carbide (272X)

temperature flashing of the filaments during exhaust would not be feasible. This limitation is the price paid for a filament feature which is very important in the design of high-power, high-frequency tubes.

All directly heated cathodes (filaments) must be so mounted that heating current can be passed through them while they are held in proper relationship to other tube elements. In any structure, the heat lost to the mounting mechanism is considerable. To offset this loss, a method known as "end-loss correction" is used on all Super-Power tubes. This correction consists simply of reducing the cross section of the filament near the ends where it is mounted. This arrangement creates sections of higher resistance in which more power is dissipated (because the current through the strand is constant). By proper design, this additional power can be made just sufficient to offset the heat lost to the mountings.

The difference between a corrected and an uncorrected filament is shown diagrammatically in Fig. 5. For a given length, much more filament area is maintained at a useful emitting temperature, or, for a given emitting surface, the tube can be made much shorter, thus greatly enhancing higher-frequency operation.

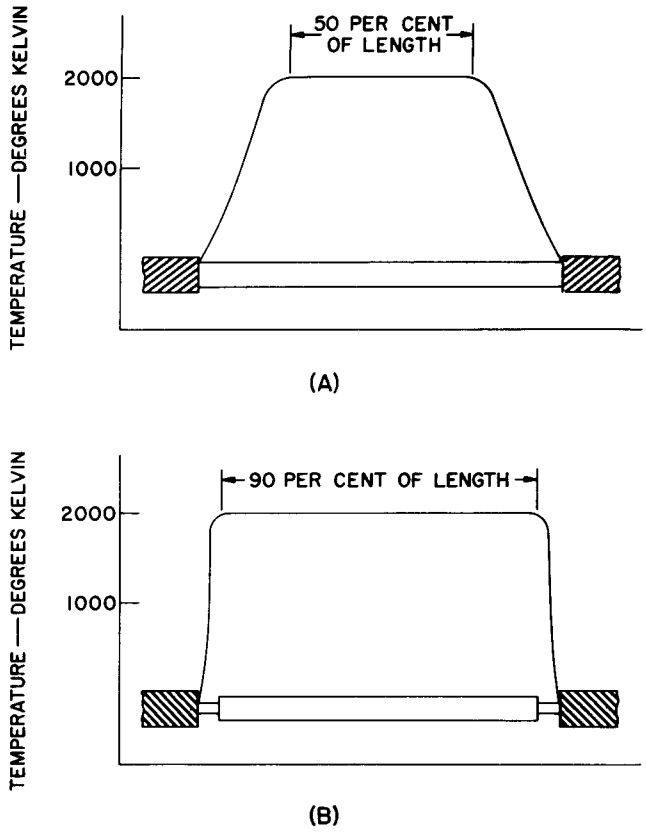


Figure 5. Temperature-Distribution Curves: (A) filament without end-loss correction; (B) filament with end-loss correction

End-loss correction, as described, is a useful tool in the design of high-power tubes. However, it must be pointed out that such a correction can be made for only one temperature. It is normal to correct for the operating temperature. At higher temperatures the thinned cross sections overheat, as shown in Fig. 6. Obviously, such a filament, properly corrected for operating temperature, cannot be flashed at high temperatures during exhaust, without melting the ends.

Preferred Carburization

Experiments have shown that a thoriated-tungsten filament can be carburized directly to the laminated phase in a hydrogen-hydrocarbon atmosphere, and that

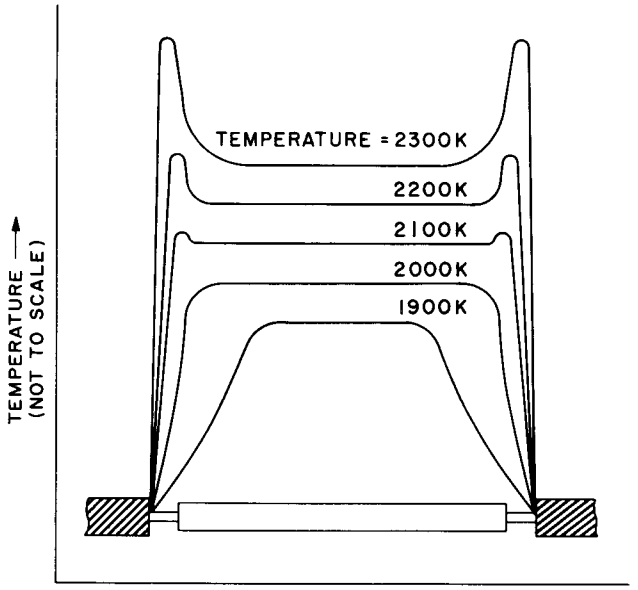


Figure 6. Effect of Various Center Temperatures on a Filament Having End-Loss Correction for an Operating Temperature of 2000 K.

a filament so produced will have full, stable emission at operating temperature without further high-temperature activation. In this method, jets of pure hydrogen are directed at the reduced-area end sections to keep them from burning out or carburizing during the process. The carburizing schedule used on this type of filament is shown in Fig. 7.

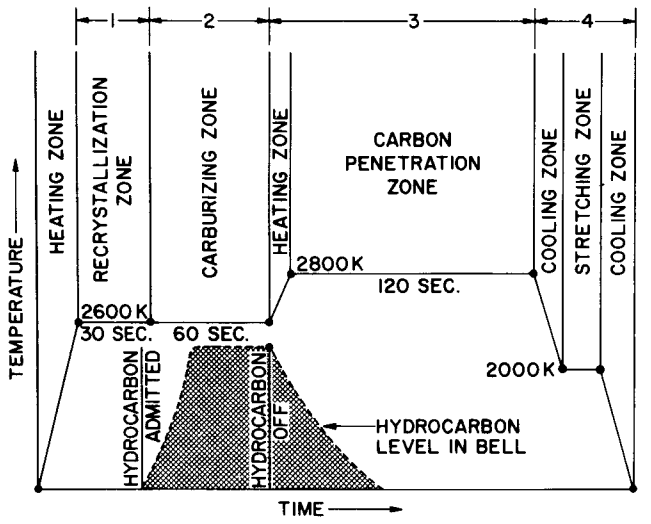


Figure 7. Typical Cycle for Carburizing Filaments

This carburizing process involves four steps: (1) the filament is flashed at a high temperature in pure hydrogen to cause recrystallization and to reduce the thoria to thorium metal; (2) a closely controlled hydrogen-benzene mixture is admitted while the filament is still hot (this step forms a thin rind of massive-type carbide); (3) the flow of benzene is turned off so that no additional carbon is available, and the temperature is increased so that the carbide already formed penetrates deeper and produces the carbon-starved conditions that yield the proper laminated carbide; (4) the filament is stretched approximately one per cent beyond the elastic limit at 2000 K. The stretching step, possible only on straight wire, not only produces a straight filament, important in electron-optical devices, but also appears to enhance electron emission, possibly by pulling apart the grains slightly and allowing more freedom for thorium migration.

Filaments produced by this schedule are presently used in tubes which have been operated more than 20,000 hours without loss of emission. Checks of the carbide have indicated that half of the carbide still remains for future life.

Some Precautions for Carburization

A word of caution must be given regarding the setting up of carburizing schedules. The filament being carburized must be heated in a clean atmosphere, after which the carbon can be added to enter into the reaction. When the filament is heated in a hydrogen-hydrocarbon atmosphere, the hydrocarbon dissociates long before any reaction between the tungsten and carbon occurs. A carbon deposit then forms on the surface which greatly increases the thermal emissivity so that for a given power input the temperature is quite low. In addition, it acts as a shield to prevent additional carbon from reacting with the tungsten. For these reasons, the filament is flashed in pure hydrogen first and held at temperature while the hydrocarbon is added.

The foregoing procedure is recommended; however, particular attention must be paid to all operating conditions because the process is very critical. The amount of hydrocarbon vapor must be closely controlled, all times and temperatures in the process must be held accurately, and the hydrogen must be pure and extremely dry to prevent any reaction with the monolayer of thorium or with the carbide.

Quality Control

The quality of filaments produced by the preceding method is controlled in several ways. The decrease in current (or increase in voltage) indicates the change in resistance during carburization and is one of the conditions kept constant. With many production tubes, thyratrons are used to shut off the heat when the proper resistance is reached. However, resistance is only one factor and can change with surface condition, as pointed out by Horsting[27]. A second check can be made by weighing the filaments before and after carburizing to determine whether they have reacted with the correct amount of carbon. Two types of destructive tests are used, on a sampling basis, to assure the correct carbide structure and thickness. The sample filaments are sectioned and viewed through the metallurgical microscope to study the carbide structure

and measure the layer thickness. In addition, sections of the filaments are placed in a spectrograph and their surfaces explored for thorium. A properly activated filament shows traces of thorium when the surface is arced in a spectrograph.

Electron-emission tests are also made in either finished tubes or in test bottles which have been properly baked and processed, and total space current is plotted against voltage. Fig. 8 shows a plot of voltage and current on a typical RCA Super-Power tube. In Fig. 8, the point where the current begins to break away from the 3/2-slope of the voltage indicates the maximum space-charge-limited emission available.

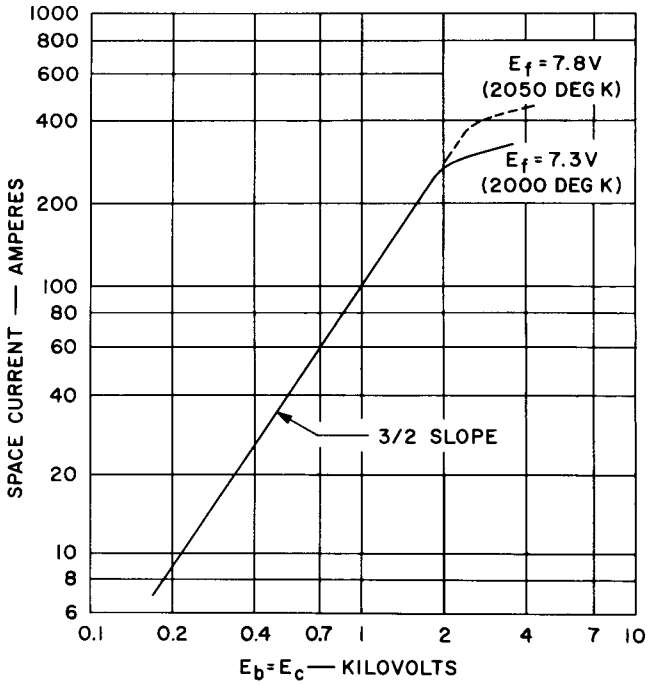


Figure 8. Typical Emission Test of RCA Super-Power Tube; Break-Away Points Indicate Where Cathode Becomes Temperature-Limited

In Fig. 9, a plot of emission versus temperature is shown together with data on the radiation and emission efficiency. Most large power tubes are designed to operate at a filament temperature of 2000K which yields about 3 amperes of emission per square centimeter of emitting area.

Fig. 10 shows curves for use in converting brightness temperature, as read on an optical pyrometer, to true temperature. These curves, which are based on the emissivity of pure tungsten and carburized tungsten, are taken from published literature[29] and hold true for most cases. The curve shown in Fig. 10B shows recent measurements of the spectral emissivity of cathodes used in certain Super-Power tubes. It can be seen that this curve differs slightly from that shown in Fig. 10A. More accurate results can be obtained by measuring the spectral emissivity for each type of cathode to account for surface differences.

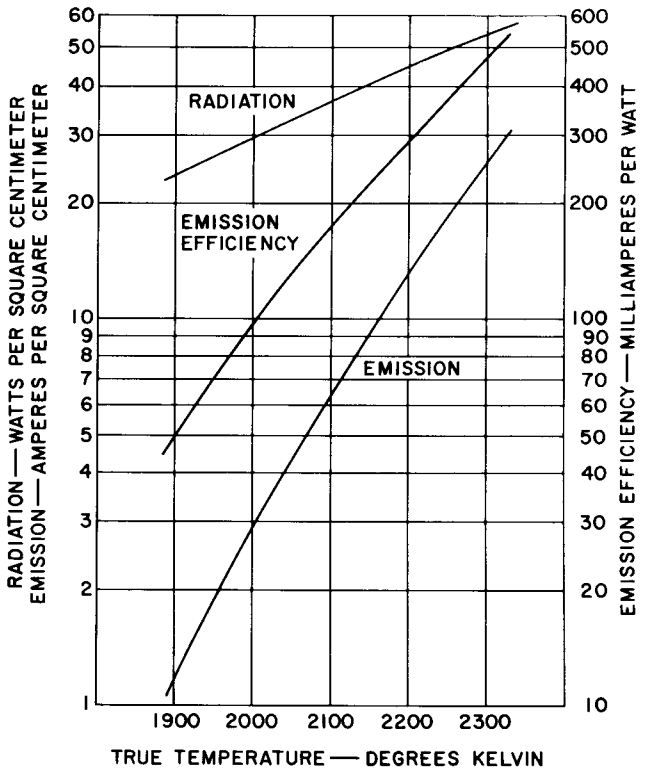


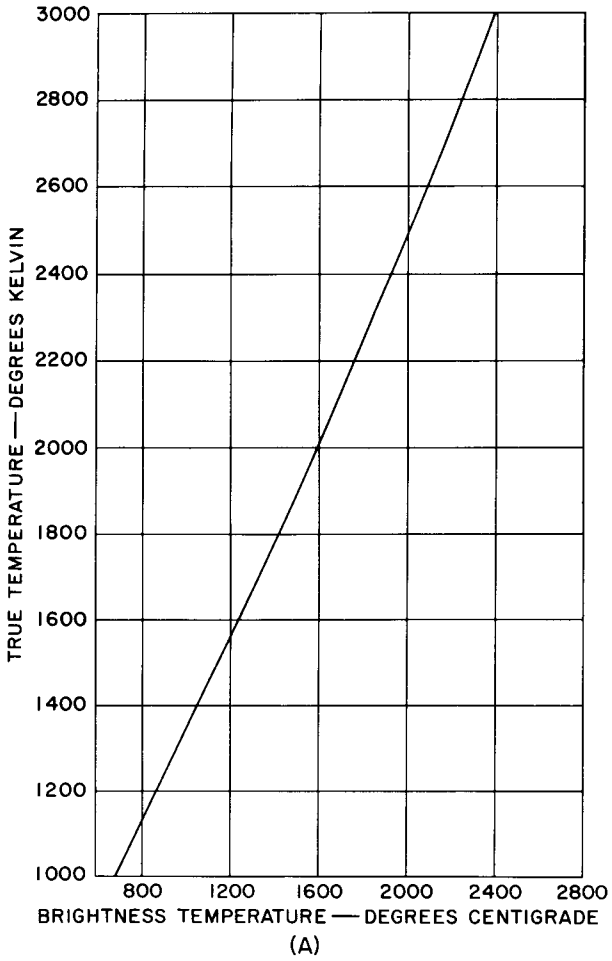
Figure 9. Variation of Emission, Emission Efficiency, and Radiation of Thoriated Tungsten as a Function of Temperature

THORIA EMITTERS

Because thoriated tungsten had proved so attractive as an emitter of electrons, a substantial program was conducted from 1940 to 1950 to achieve electron emission directly from thorium oxide. Thoria has three inherent advantages over thoriated tungsten. First, more shapes of tube elements are possible because of the ease of working the base metals to which thoria is applied. Second, higher emission densities seem possible with thoria, although this increase may be due to the increased surface area. Third, thoria cathodes are easy to activate and are less susceptible to poisoning. They appear to be extremely rugged and continue to emit electrons after treatments which completely kill thoriated tungsten or barium-strontium oxide.

Thorium-oxide powder (ThO_2) is usually coated on a refractory base metal such as tungsten (W), tantalum (Ta), or molybdenum (Mo) by painting, spraying, or cataphoresis. The base metal reduces some of the thorium oxide to thorium, which then diffuses to the surface. Emission occurs from a monolayer in a manner similar to that of thoriated tungsten.

Forgue[30] experimented with many combinations of metal powders sintered to a base metal and coated with thoria (THO_2 on W on Ta, ThO_2 on Mo on Ta, ThO_2 on W on Mo, etc.). A tantalum base metal was preferred because it could be shaped easily; the recommended cathode at that time was ThO_2 on Mo on Ta. Fig. 11 compares Forgue's emission data for two experimental thoria combinations with that for pure tungsten, pure tantalum, and thoriated tungsten.



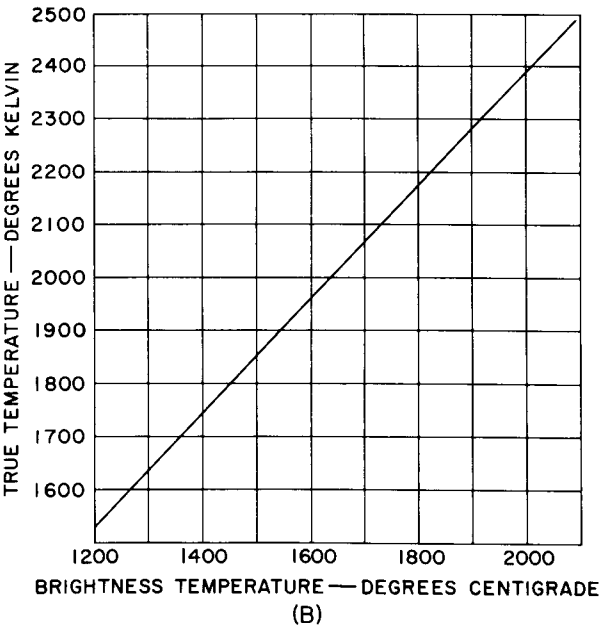


Figure 10. Curves for Conversion of Brightness Temperature to True Temperature: (A) pure tungsten (for carburized tungsten, curve is about 10 degrees below that shown and parallel to it); (B) carburized thoriated tungsten (as measured on a super power tube)

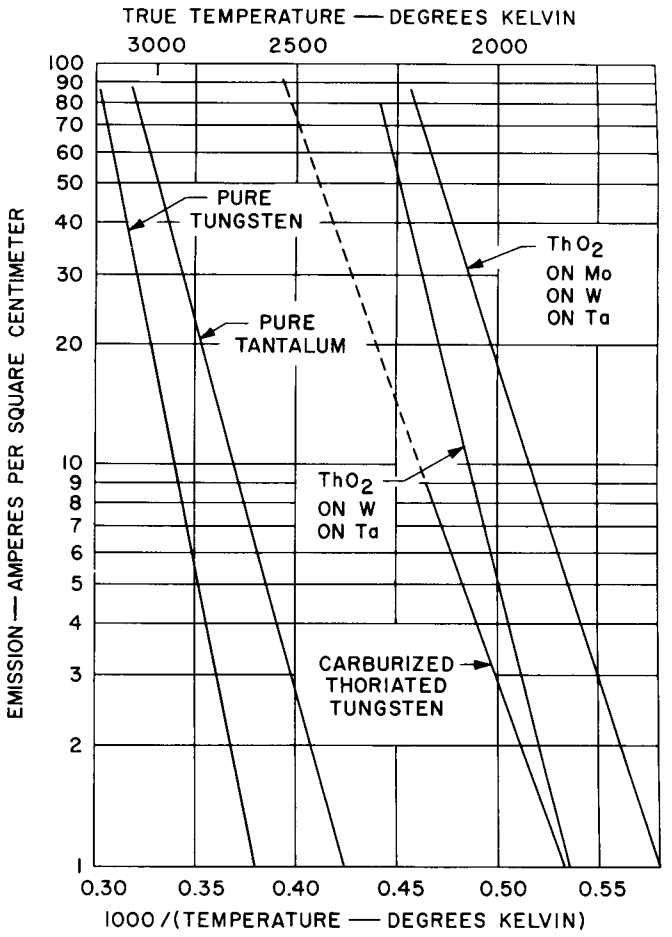


Figure 11. Comparison of Thoria Emission-Temperature Data (from Forgue) with Data for Standard Cathodes

Thoria cathodes have not proved to be the panacea once expected. The principal difficulty has been in keeping the thorium oxide on the base metal. The oxide is not only difficult to keep on mechanically, but is also easily ripped loose under severe ion bombardment.

The solution to these mechanical problems may be in the area of "cermet" or "dispenser" type cathodes. Tubes have been made with directly heated thoria cathodes pressed into cylindrical form and made conductive by addition of tungsten or molybdenum powder to the thoria before pressing [31].

Thoriated tungsten is still the more reliable emitter although, with further effort, thorium oxide may well displace it in the future. At present, only one commercial RCA tube employs the thoria cathode: the 8D21 vhf television tetrode. Life and reliability now appear to be excellent on this tube type, although early production was beset by many cathode difficulties. Thoria cathodes have many attractive attributes. It is possible that matrix technique, where the emissive material is held within a porous metal layer, may well improve the mechanical structure to the point where thoria will become a reliable cathode material.

SUMMARY

Pure-tungsten cathodes are no longer being designed into high power electron tubes. The penalty paid for high cathode heating power is no longer justified since thoriated-tungsten emitters have been improved to the point where reliable operation in even the highest power tubes is now possible. Thoriated tungsten must be properly made and the processing carefully controlled to achieve the proper grain structure and carbide layer for full uniform electron emission under extreme voltage conditions. Although thoriated tungsten is used almost universally in all high-power electron tubes, thoria-coated cathodes have excellent possibilities and may, in the future, displace thoriated tungsten as the preferred high-power emitting material. Many problems are yet to be solved to advance the state of the art of this material; however, there is no fundamental reason why it should not be the cathode material of the future.

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