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PROCESS OF CARBURIZING

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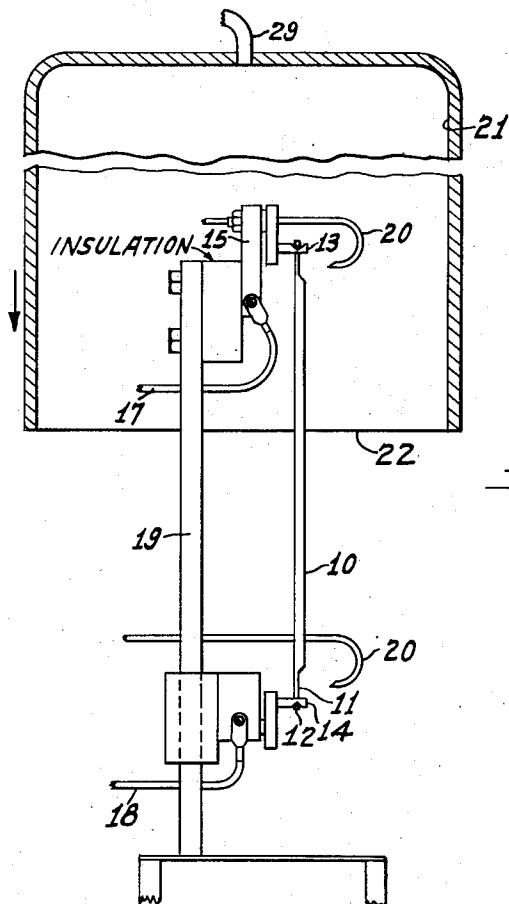


Fig. 1

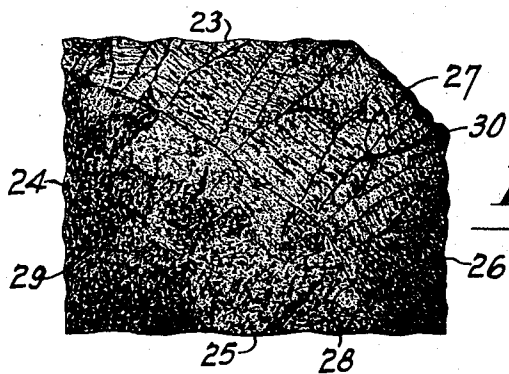


Fig- 2

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PROCESS OF CARBURIZING

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10 Claims. (Cl. 148—13.1)

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This is a continuation-in-part of my co-pending application, Serial No. 165,093, filed May 29, 1950, now abandoned.

My present invention relates to the carburizing of metallic surfaces and more particularly to a process for carburizing the surfaces of thoriated tungsten electrodes of the type used in electron discharge devices.

In the manufacture of electron discharge devices, particularly those designed for high power output considerable difficulty has been met in obtaining carburized thoriated tungsten electrodes having uniformly satisfactory characteristics. One serious disadvantage in the manufacture of such electrodes has been the poor and unstable emission obtained. Other disadvantages of processes in use have to do with the wide variation in the characteristics of both the electrodes and the tubes in which they are incorporated. Since such devices often use extremely high values of voltage and current the foregoing critically affect satisfactory operation thereof.

It has been found that the tungsten carbide layer on thoriated tungsten electrodes may vary in crystalline structure from a massive phase corresponding to WC to a second massive phase corresponding to W₂C and then through a laminated phase in which the carbon concentration by weight per cent varies from 3.16 to approximately 2.45. In general, there was found to be an abrupt line between the WC phase, 6.12 per cent carbon, and the massive W₂C phase, 3.16 per cent carbon. As indicated in the article "Carbide structures in carburized thoriated tungsten filaments," C. W. Horsting, Journal of Applied Physics, vol. 18, No. 1, p. 95, January, 1947, the laminated phase has been found to be the preferred form of tungsten carbide for thoriated tungsten emitters. However, known processes of carburizing have failed to produce uniform results and have required costly activation at high temperatures after the emitter has been mounted in an electron discharge device.

A principal object of my invention is the provision of a process for manufacturing carburized electrodes having improved and stable emission.

Another object is the provision of an improved process for pre-carburizing thoriated tungsten electrodes.

A further object is the provision of a process for pre-carburizing thoriated tungsten electrodes which insures the formation of the desired crystalline phase.

Yet another object is the provision of such a

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method for pre-carburizing which permits the use of preferred electrode shapes and structures which will have full stable emission at the operating temperature without requiring high temperature activation after it is mounted in a vacuum tube.

Still another object is the provision of a process for pre-carburizing thoriated tungsten electron emitters and forming a preferred tungsten carbide layer having a laminar structure.

In carrying out one embodiment of my novel process, I have heated a thoriated tungsten electrode in an inert atmosphere to recrystallize the tungsten. Then while maintaining the temperature of the electrode I have introduced hydrocarbon vapor into the atmosphere. The hydrocarbon vapor content of the atmosphere was maintained while the temperature of the electrode was maintained for a desired period of time. I have then raised the temperature of the electrode, cut off the supply of the hydrocarbon vapor, and maintained the electrode at the elevated temperature in the atmosphere in which the hydrocarbon vapor concentration was rapidly being depleted. I have found the carburized thoriated tungsten emitters thus formed to have the desired laminated phase crystalline structure. Such electrodes give uniform stable electron emission at the operating temperature without requiring further activation treatment.

The novel features which I believe to be characteristic of my invention are set forth with particularity in the appended claims. The invention itself will best be understood by reference to the following description taken in connection with the accompanying drawing in which:

Figure 1 is a semi-diagrammatic view of an apparatus for carrying out my invention; and

Figure 2 is a reproduction of a photomicrograph showing a segment of a thoriated tungsten electrode magnified 400 times.

I preferably carry out my process and carburize the electrodes prior to assembling the same in the mount or supporting structure because of advantages which are gained as will be pointed out. However, my process is not limited to pre-carburizing and also lends itself to the carburizing of electrodes after they are incorporated in the mount structure of an electron discharge device and provides greatly improved electrodes.

In Figure 1 I have illustrated one form of apparatus which I have conveniently used to pre-carburize a thoriated tungsten electron emitter or electrode 10 having reduced portions 11 which function as heat loss correction means and

mounting heads 12. Electrode 10 is conveniently mounted by means of its mounting heads 12 between two slotted and grooved supports 13, 14 which are each supported from electrically conductive members 15, 16 in any suitable manner. Members 15 and 16 are connected to the terminals of a source of electrical power (not shown) by leads 17, 18. Member 15 is insulated from standard 19 and supported thereon. Member 16 is conveniently slidably connected to standard 19 in such manner as to permit axial elongation of electrode 10 when heated.

Cooling means in the form of tubes 20 connected to a controlled source of dry hydrogen direct the coolant which is inert with respect to thoriated tungsten, at reduced portions 11 and serve to maintain portions 11 at a sufficiently low temperature to prevent their burning out or being carburized.

Bell 21 is movably mounted and may be lowered around standard 19 and the parts supported thereon with its lower end 22 open to the atmosphere if a light gas is used; with a heavy gas, filling from the bottom would be necessary. Tubing 29 opens into bell 21 and is connected to controlled sources of gases to be introduced into the bell to form an atmosphere most favorable to carburizing.

As pointed out above, it has been found that the laminated phase of the tungsten carbide structure is that desired while the massive WC and W₂C represent undesirable constituents and are to be avoided if the desired emitter is to be obtained. In Figure 2 is shown a segment of a carburized thoriated tungsten electrode as reproduced from a photomicrograph and is a magnification of 400 times. All of the lines 23-26 represent boundaries of the photomicrograph while surface 27 is a reproduction of a portion of the outer surface of the electrode. Line 28 running through the specimen shows the sharp interface between the core and the carbide in the finished product. Core 31 has as shown the recrystallized structure of thoriated tungsten while the laminated phase of tungsten carbide is clearly apparent in the region 30 between interface 28 and exterior surface 27.

In accordance with my improved process I consistently form the preferred laminated phase of tungsten carbide ranging from 3.16 to 2.45 per cent carbon. To attain these results I have found it to be essential that the temperatures, hydrocarbon vapor concentration and duration of heating be critically controlled. If the temperature to which the electrodes is heated is too low, a shell of carbon forms on the thoriated tungsten electrode which gives it undesirable characteristics. If the temperature is too high, the depth of penetration of the carbide may be excessive while a surface layer of decarburized thoriated tungsten may be formed depending upon the carbon content. Too great a concentration of hydrocarbon vapor prevents the formation of the preferred laminated phase and results in either the massive W₂C or WC phases. Too small a concentration generally results in a decarburized or carbon-starved surface layer with an internal layer of the carbide which does not reach the surface. The length of the heating time interval is also critical. If heating is too prolonged carbide penetration will be excessive. Since tungsten carbide is extremely brittle this condition must be avoided. On the other hand, if the heating period is too short the depth to which the electrode is carburized will be insufficient to pro-

duce the desired effect. The carburizing reaction is extremely rapid at elevated temperatures and must be carefully regulated.

I have found that an initial heat treatment of approximately 20 to 40 seconds at a temperature between 2575 degrees and 2625 degrees K. serves to recrystallize and stabilize the tungsten sufficiently to aid in obtaining a much more uniform product. This is carried out in an inert atmosphere. By inert or inert atmosphere, I wish it to be understood here, as elsewhere, that the gas or vapor does not react unfavorably with thoriated tungsten and is substantially inert with respect thereto. Though the heat treatment is highly beneficial, it is not essential and may be omitted.

On completion of the recrystallization and without allowing the electrode to cool hydrocarbon vapor is admitted by introducing a gas mixture of hydrocarbon with an inert gas. Heating of the electrode is continued at a temperature between 2575 degrees and 2625 degrees K. for one minute. During this interval the hydrocarbon is broken down to hydrogen and carbon; the carbon combining with the hot tungsten to form a surface layer of tungsten carbide. This carbide is of the massive W₂C type.

I then raise the temperature of the electrode substantially to between 2775 degrees and 2825 degrees K. and simultaneously cut off the supply of hydrocarbon vapor but continue to admit the inert gas. The electrode is maintained at this temperature for about two minutes in the rapidly waning hydrocarbon atmosphere. This insures that this part of the reaction is one which is carbon-limited. The penetration of the carbide layer becomes greater. The percentage composition of the carbide layer becomes reduced below 3.16 per cent carbon and to the range of between 2.45 and 3.16 per cent carbon; thus forming the laminated phase.

It is to be understood that substantial variations in the cross-sectional thickness of the metal being carburized may require or permit corresponding changes in the duration of the heating times; temperature being held constant. However, the variations may be readily determined.

Hydrocarbons other than benzene which may be mixed with hydrogen to form a carbon bearing vapor include acetylene, toluene, and xylene. Non-hydrocarbons which may be mixed with hydrogen to form a carbon bearing vapor include colloidal particles of carbon, aniline, and diethyl ether.

Other hydrocarbon and non-hydrocarbons may be mixed with the hydrogen to form a carbon bearing vapor provided they vaporize readily, decompose into their elements to produce free carbon at the carburizing temperature of the electrode, and do not have other elements, which adversely affect the electrodes being carburized.

As a specific example, thoriated tungsten electrodes 10 have been mounted in the apparatus of Figure 1 and pre-carburized. Electrodes 10 were substantially trapezoidal in cross section having a width of .057 inch narrowing to .040 inch with the narrow face rounded. The thickness from front to rear was .037 inch. The electrode was approximately 8.6 inches long. The reduced portions 11 are cooled by jets of pure dry hydrogen as shown in Figure 1. Bell 21, 24 inches high and 14 inches in diameter, was lowered and the electrode heated for thirty seconds at 2600 degrees K. in an atmosphere of pure dry hydrogen which was continuously flushed through the bell at the rate of 40 cubic feet per hour; the end

22 of the bell being open to the atmosphere. Then while maintaining the electrode at the temperature of 2600 degrees K. hydrocarbon vapor was admitted by adding a flow of 12 cubic feet per hour of hydrogen carrying benzene vapor to the 40 cubic feet per hour of pure hydrogen which was flowing through the bell. The electrode was maintained at a temperature of 2600 degrees K. for a period of one minute.

I formed the benzolated hydrogen by passing the 12 cubic feet per hour of hydrogen first through a dryer and then through an atmosphere of benzene vapor in a carburetor. The carburetor had an internal diameter of $4\frac{1}{2}$ inches with a pool of benzene at room temperature. The hydrogen inlet and outlet are both .200 in. internal diameter tubing with their openings 5 inches above the surface of the benzene. The walls of the carburetor extend four inches above the surface of the benzene and then taper inward at an angle of about 45 degrees.

The source of hydrocarbon is then cut off and with the flow of the hydrogen maintained, the electrode was then simultaneously held at a temperature of 2800 degrees K. for two minutes.

Cathodes having thoriated tungsten emitters carburized by my process have uniform stable electron emission at the operating temperature of 2000 degrees K. and do not require further activation. Though I have described my novel process in connection with one specific type of cathode element which is particularly useful in super power devices, cathodes have also been successfully made in accordance with my process having entirely different shapes or structures. In such case, the duration of the heating is modified in accordance with the cross-sectional thickness of the cathode or elements and the extent of carbide penetration desired. Though gases or vapors other than hydrogen or benzene may be used, I prefer these as most consistently providing a uniform stable electrode. It is apparent, therefore, that many variations may be made without departing from the scope of my invention as set forth in the appended claims.

I claim:

1. The process of carburizing a thoriated tungsten element, comprising heating the thoriated tungsten element in a carburizing atmosphere containing inert gas and hydrocarbon vapor at sufficiently high temperature to decompose the hydrocarbon, and then continuing the heating of the thoriated tungsten element at a higher temperature in an atmosphere in which the hydrocarbon content is rapidly decreasing.

2. The process of carburizing a thoriated tungsten element, comprising heating the thoriated tungsten element to a predetermined temperature in an atmosphere containing inert gas to which hydrocarbon vapor is being continuously added, and then stopping the addition of the hydrocarbon vapor and continuing the heating of the thoriated tungsten element at a higher temperature in said atmosphere in which the hydrocarbon content is rapidly decreased.

3. The process of carburizing a thoriated tungsten element, comprising heating the thoriated tungsten element in an inert atmosphere at a predetermined temperature and stabilizing the crystalline structure, then while continuing to heat said element at said temperature adding hydrocarbon vapor to said atmosphere said temperature being sufficiently high to decompose the hydrocarbon to create and maintain a carburizing atmosphere, and finally discontinuing the ad-

dition of hydrocarbon vapor and continuing to heat said element at a substantially higher temperature while the hydrocarbon vapor content of the atmosphere is rapidly being depleted.

4. The method of carburizing a thoriated tungsten element, comprising heating said thoriated tungsten element at a predetermined temperature in a carburizing atmosphere to which carbon bearing vapor is added to maintain the carbon concentration and forming a layer on said element which is substantially the massive phase W_2C , said temperature being high enough to decompose said vapor and then reducing the addition of carbon bearing vapor and continuing to heat said element in said atmosphere in which the carbon content is rapidly reduced and converting substantially all of said W_2C to the laminated phase.

5. The method of pre-carburizing a thoriated tungsten element, comprising heating said thoriated tungsten element at a predetermined temperature in an atmosphere containing inert gas to which carbon bearing vapor is being added and forming a surface layer of a predetermined thickness which is substantially entirely massive phase tungsten carbide on said element, said temperature being high enough to decompose said vapor and then decreasing the addition of carbon bearing vapor and continuing to heat said element in said atmosphere the carbon content of which is rapidly decreasing and converting substantially all of said massive phase tungsten carbide to a layer of greater thickness of substantially all tungsten carbide of laminated phase.

6. The method of pre-carburizing a thoriated tungsten element having a portion of reduced thickness, comprising heating said thoriated tungsten element at a predetermined temperature in an atmosphere containing inert gas to which carbon bearing vapor is being added and forming a surface layer on said element which is substantially all massive phase tungsten carbide while preventing the formation of such a layer on said portion of reduced thickness, said temperature being high enough to decompose said vapor and then reducing the addition of carbon bearing vapor and continuing to heat said element at a higher temperature in said atmosphere in which the carbon content is rapidly reduced and converting substantially all of said tungsten carbide to the laminated phase, while at the same time continuing to prevent the formation of a carbide layer on said reduced portion.

7. The method of carburizing a thoriated tungsten element, comprising heating said thoriated tungsten element to a temperature between 2575 degrees K. and 2625 degrees K. in an atmosphere containing an inert gas and to which a hydrocarbon vapor is being added and forming a surface layer on said element of predetermined thickness which is substantially entirely massive phase W_2C on said element, and then stopping the addition of hydrocarbon vapor and heating said element to a temperature between 2775 degrees K. and 2825 degrees K. in said atmosphere, the hydrocarbon content of which is rapidly decreasing and converting substantially all of said layer of W_2C to a layer of greater thickness of laminated phase W_2C .

8. The method of carburizing a thoriated tungsten element comprising heating said thoriated tungsten element to a temperature between 2575 degrees K. and 2625 degrees K. in an atmosphere containing dry hydrogen and to which benzene vapor is being added and forming on said ele-

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ment a surface layer of predetermined thickness which is substantially entirely massive phase W_2C , and then stopping the addition of benzene vapor and heating said element to a temperature between 2775 degrees K. and 2825 degrees K. in said atmosphere the benzene vapor content of which is rapidly decreasing and converting substantially all of said layer of W_2C to a layer of greater thickness of laminated phase W_2C .

9. The method of carburizing a thoriated tungsten element comprising heating said thoriated tungsten element to a temperature of about 2600 degrees K. in an atmosphere containing dry hydrogen and to which benzene vapor is being added and forming on said element a surface layer of predetermined thickness which is substantially entirely massive phase W_2C , and then stopping the addition of benzene vapor and heating said element to a temperature about 2800 degrees K. in said atmosphere the benzene vapor content of which is rapidly decreasing and converting substantially all of said layer of W_2C to a layer of greater thickness of laminated phase W_2C .

10. The method of pre-carburizing a thoriated tungsten element having a portion of reduced thickness, comprising heating said thoriated tungsten element at a predetermined temperature in

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an atmosphere containing inert gas to which carbon bearing vapor is being added and forming a surface layer on said element which is substantially all massive phase tungsten carbide while cooling said portion of reduced thickness and preventing the formation of such a layer on said portion of reduced thickness, and then reducing the addition of carbon bearing vapor and continuing to heat said element at a higher temperature in said atmosphere in which the carbon content is rapidly reduced and converting substantially all of said tungsten carbide to the laminated phase, while at the same time, continuing to prevent the formation of a carbide layer on said reduced portion.

WILLIS E. HARBAUGH.

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