Feb. 24, 1970 F. H. HORN 3,497,755

VACUUM DEVICES WITH ELECTRODE MEMBERS CONTAINING OXYGEN-REACTIVE MINOR CONSTITUENT

Filed July 1, 1966 2 Sheets-Sheet 1

Fig. 1.

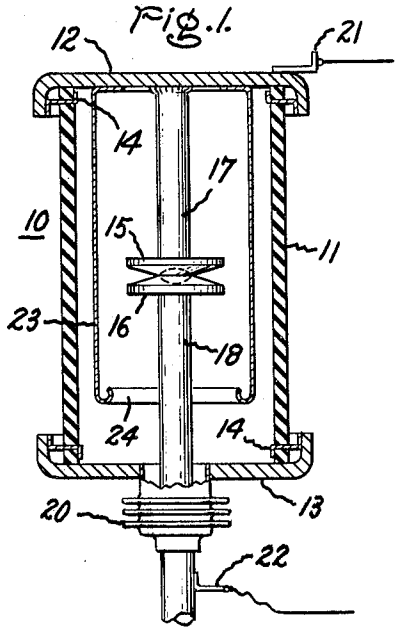

Fig. 2.

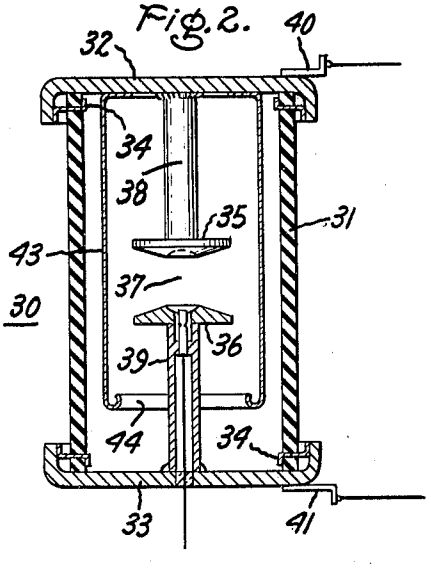

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Fig. 3.

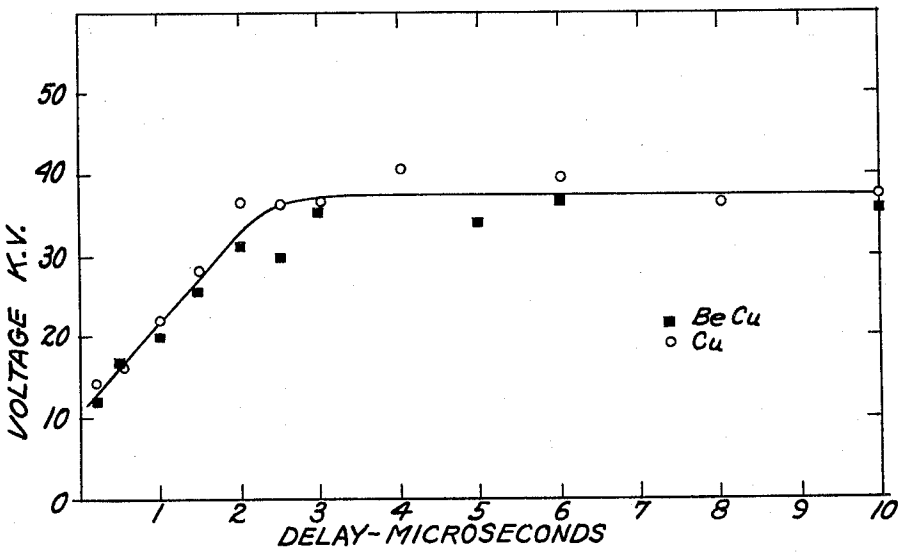
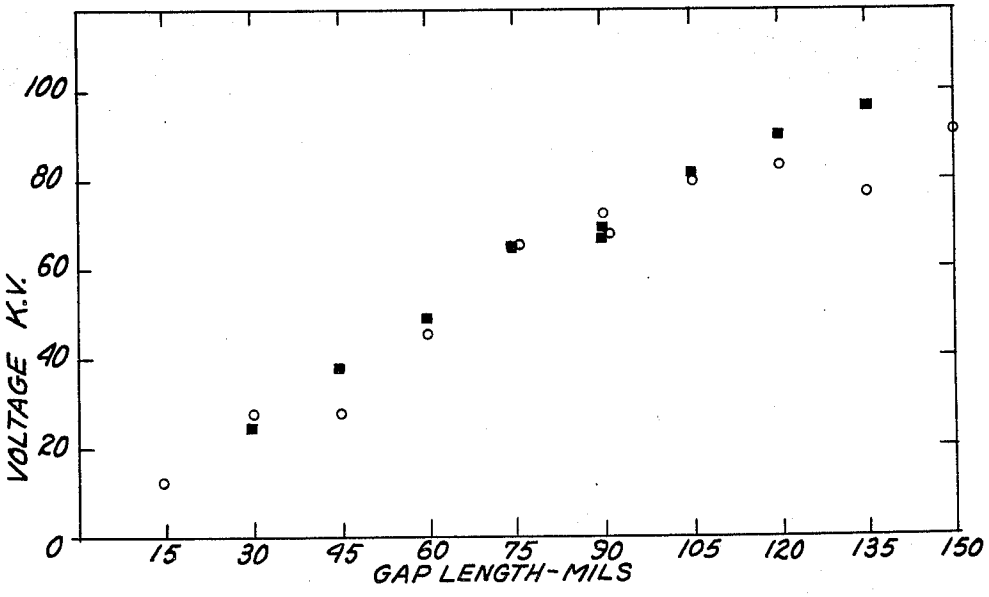


Fig. 4.



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3,497,755

VACUUM DEVICES WITH ELECTRODE MEMBERS CONTAINING OXYGEN-REACTIVE MINOR CONSTITUENT

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U.S. Cl. 313—311 9 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to vacuum gap devices as for example vacuum switches and triggered vacuum gap devices having improved electrode members which are free of sorbed gasses and constituents which, upon arcing, are capable of releasing gasses and to novel methods of the preparation thereof. More specifically the present invention relates to devices of the aforementioned type containing copper or other metallic electrodes which are rendered free of gas and gas-forming impurities by a relatively simple and inexpensive technique.

Within the last decade a resurgence of the importance of vacuum switches and vacuum gaps has occurred. This resurgence has been a result, in part, of substantially improved technologies for the formation of vacuum envelopes capable of withstanding the pressures and temperatures of repeated arcing at high voltages and currents over long periods of time and to the development of unique and novel choices of materials as for example, the high vapor pressure arc-electrode materials set forth in Lee et al. Patent No. 2,975,256 and Lafferty Patents Nos. 2,975,255 and 3,016,436. In the case of fixed gap devices, great improvement has followed the development of the triggered vacuum gap as described and claimed in Lafferty Patent No. 3,087,092.

In devices of the classes represented by the aforementioned patents, there is a common denominator in that successful operation depends upon the attainment of essentially absolute freedom from gas of the metal which composes that portion of the electrode upon which the footpoints of an arc stricken therebetween may rest. It has been found by experimental evidence that if the arc-electrode, or region of the arc-electrode upon which the footpoints are located, contains sorbed gasses or constituents which, upon the melting and vaporization of the arc-electrode material, decompose to form ionizable gasses, the residual pressure within the arc device rises and extinction of the arc upon the occurrence of a first current zero of alternating current does not occur.

Accordingly it is a principal object of the present invention to provide vacuum devices of the vacuum switch and vacuum gap types in which high vacuum is readily maintained by the use of electrodes that are essentially free of all gas and gas-forming constituents.

A further object of the present invention is to provide vacuum gap devices capable of maintaining high vacua during arcing conditions without expensive, complicated, and time-consuming processing of the constituents thereof.

Still another object of the present invention is to provide arc-electrodes for vacuum gap devices which are inexpensive to construct, easily fabricated from readily available material, and which are essentially free of gas and gas-forming constituents.

Yet another object of the present invention is to provide methods of forming high quality, low cost vacuum gap devices capable of interrupting high voltages at high current ratings in repetitive use without the use of expensive fabrication techniques.

Briefly stated, in accordance with one aspect of the present invention, I provide a vacuum gap device including a pair of oppositely disposed arc-electrodes defining therebetween a breakdown gap and located within an hermetically sealed envelope which is evacuated to a pressure of at least 10^{-4} mm. of mercury pressure or lower and preferably lower than 10^{-5} mm. Hg and means for connecting the respective electrodes to an electrical circuit to be protected or controlled thereby. In one embodiment of the invention at least those portions of the arc electrodes which are to be arcing surfaces and which are adapted to support the footpoints of an electric arc therebetween are composed of a high vapor pressure metallic constitutent which is free of all gas and gas-forming impurities, particularly of oxygen and is rendered such by the incorporation therein of a small but finite quantity of a metal which has a great affinity for oxygen and forms therewith a high temperature-stable oxide which precludes oxygen from affecting the vacuum within the device and thereby adversely affecting its operating characteristics. I have found in particular that beryllium is outstanding for such purification of the electrode material.

In one embodiment of the present invention the two arc-electrodes are fixed to define a fixed gap therebetween and a separately-connected trigger electrode assembly is juxtaposed immediately adjacent the gap and adapted to inject an electron ion plasma thereinto to facilitate breakdown thereof. In accord with another embodiment of the present invention one electrode is fixed and the other is movable to cause the formation of a vacuum switch or arc interrupter device.

The novel features believed characteristic of the present invention are set forth in the appended claims. The invention itself, however, together with further objects and advantages thereof may best be understood by reference to the following description taken in connection with the appended drawing in which:

FIGURE 1 is a vertical cross-sectional view of a schematically illustrated vacuum circuit interrupter in accord with one embodiment of the invention,

FIGURE 2 is a vertical cross-sectional view of a schematically illustrated fixed-gap vacuum gap device constructed in accord with another embodiment of the present invention, and

FIGURES 3 and 4 are graphical representations of the comparable recovery strength and impulse breakdown characteristics, respectively, of devices constructed in accord with the present invention utilizing the electrodes thereof and of comparable prior art devices utilizing conventional electrodes.

In FIGURE 1 an interrupter chamber **10** comprises a sidewall member **11** which may be cylindrical in shape and is preferably constructed at least in part of a suitable insulating material, having at the ends thereof a pair of metallic end wall members **12** and **13** enclosing the volume therein to form an interrupter chamber which is hermetically sealed. Suitable seal members **14** are provided connecting sidewall member **11** and end-wall members **12** and **13** to facilitate hermetic sealing. Alternative to the utilization of a completely insulating member **11**, the entire envelope may be substantially constructed from a metallic member, with the exception that at least one portion thereof must be of a high voltage, vacuum tight dielectric insulating material, sufficient to electrically insulate those portions of the envelope connected with one arc-electrode from those portions of the envelope connected with the other arc-electrode at very high voltages. Such interposed dielectric high-voltage insulators may be located in a variety of places, as for example along a portion of cylindrical sidewall member **11** or, alternatively, as a portion of the end-wall members **12** or **13**. Irrespective of where the insulating dielectric material

is located, an appropriate shield member must be interposed between the arcing space or gap between the arcing space or gap between the arc-electrodes and the dielectric, and preferably a series of baffle shields should be included to preclude shorting of the dielectric and rendering the device inoperative.

A pair of separable contacts or primary arc-electrodes **15** and **16**, shown in their closed circuit or circuit-making position, are located within chamber **10**. Arc-electrode **15** is a stationary member suitably attached electrically and mechanically to a conducting arc-electrode support rod **17** which, at its upper end, is united electrically and mechanically with end-wall member **12**.

Arc-electrode **16** is mounted upon and electrically united with a suitable conducting arc-electrode support rod **18** and is movable, being connected to bellows **20** or an equivalent vacuum-tight flexible member, permitting reciprocating motion. Arc-electrode support rod **18** projects through a suitable aperture in end-wall member **13**, and suitable actuating means may be connected thereto to cause a reciprocating motion of rod **18**, facilitating the entry of arc-electrode **16** into, and removal from, engagement with arc-electrode **15**. The electrical circuit which is to be protected or controlled by the arc-interrupter may be completely by making suitable connections to terminal **21**, electrically and mechanically mounted upon end wall member **12**, and terminal **22**, electrically and mechanically connected to rod **18**. Such connection may either be in series or parallel circuit relationship with a load depending upon the particular manner in which the circuit interrupter device is to be utilized.

As mentioned hereinbefore, a suitable insulator shield such as metallic cylindrical member **23**, capped with an arc-preventing ferrule **24** is interposed between arc-electrodes **15** and **16** and insulator **11** to prevent the latter from being coated with metallic particles and becoming electrically short-circuited.

The volume within vacuum interrupter chamber **10** is suitably evacuated through an exhaust tubulation (not shown) during the final assembly thereof. For proper operation of the interrupter as a vacuum-type interrupter of alternating currents the pressure within chamber **10** must be maintained at a pressure of no greater than 10^{-4} mm. of mercury and preferably a pressure of 10^{-5} mm. of mercury or less. The foregoing requirement is essential for the operation of the device as a vacuum interrupter of alternating currents. This requirement is necessary because, in order that a current carrying arc between arc-electrodes **15** and **16** be extinguished at the first-occurring current zero value, there must be substantially no ionizable gas present within chamber **10**. The occurrence of such ionization may be substantially prevented if all possible breakdown paths between arc electrodes **15** and **16** and their respective supports, are small with respect to the mean free path of an electron within the atmosphere obtained within the device. This means free path is designated as a statistical distance which an electron may travel without colliding with a gas molecule at a given pressure. These conditions may be established within the devices of the present invention only when the pressure within the interrupter chamber **10** is below approximately 10^{-4} mm. of mercury and is ensured when it is below 10^{-5} mm. of mercury.

It is not sufficient, merely to evacuate the device to the requisite vacuum initially to ensure successful operation of the device, particularly under conditions of repeated operation. In this respect, it is necessary that all possible sources of increased gas pressure during operation must be eliminated or minimized. Metallic and insulating parts may release gas particles when heated by arcing conditions during operation. Ideally all parts should be completely out-gassed prior to assembly and thereafter as well.

One type of commercially available vacuum circuit interrupter, therefore, utilizes contacts of tungsten, molybdenum, or other refractory materials which may be baked and otherwise heat treated for a sufficiently long time and at a sufficiently high temperature to remove all sorbed gases therefrom. This prevents the entry of ionized gases from the electrode materials into the vacuum chamber due to the action of the arc. This is necessary because the vacuum arc is sustained as a conducting column by ionized metallic particles which are boiled from the electrodes, primarily the cathode. During the boiling-out process, if any sorbed gasses or unstable gas-forming constituents are present within the electrode material, gas may be freed and become ionized.

Upon the occurrence of the first current zero after establishment of an alternating current arc, the ionized metallic specie within the chamber is rapidly cooled and migrates back to the electrodes, to the shield, or to the chamber wall, is deionized and removed from the chamber, lowering the pressure. This is not, however, the case with ionizable gases which may be boiled from the electrodes. Such gases continue to remain in the chamber and raise the pressure thereof. It is for this reason that the electrodes must be purified to such an extent as to cause the presence of gas and unstable gas-forming constituents within the electrode to be low enough to allow the maintenance of a vacuum of less than 10^{-4} mm. of mercury pressure within the device.

Arc-electrode support members **17** and **18**, since they are not directly exposed to the action of the arc and do not sustain the footpoints thereof need only be of standard grade, high purity, as for example, OFHC copper or the equivalent thereof. Sidewall member **11** may conveniently be constructed of high temperature glass or may be of a gas-impervious, vacuum-tight ceramic as for example, high density alumina or a fosterite ceramic. End-wall members **12** and **13** may conveniently be constructed of stainless steel or nickle or, if a fosterite ceramic is utilized for sidewall member **11**, end-wall members **12** and **13** may be fabricated from titanium, and a metal-to-ceramic seal may be made directly between the two. Shield **23** may conveniently be constructed of stainless steel, heat treated for several hours at extremely high temperatures to the order of 1000° C. for hours to remove therefrom all sorbed gasses.

A fixed vacuum gap device constructed in accord with the present invention is illustrated in FIGURE 2 of the drawing. In FIGURE 2 of the drawing, the device envelope comprises a sidewall member **31** which may be cylindrical in shape and is constructed of a suitable insulating material having the same characteristics and composition as sidewall member **11** of the device of FIGURE 1 and closed at the ends thereof by a pair of metallic end wall members **32** and **33** which may conveniently be constructed of the same materials comprising end wall members **12** and **13** of the device of FIGURE 1. Side and end wall members enclose the volume therein and form an hermetically sealed vacuum chamber. Suitable seals **34** are provided between side wall member **31** and end members **32** and **33** to facilitate the formation of hermetic seals therebetween.

A pair of spaced arc-electrodes **35** and **36**, defining therebetween a breakdown gap **37**, are disposed within envelope **30** and are supported respectively upon arc-electrode support rods **38** and **39**, which are electrically and mechanically connected with the respective end wall members **32** and **33**. An electrical circuit which is sought to be protected or controlled by vacuum gap device **30** is connected to end wall members **32** and **33** in series or parallel circuit, as desired, by means of connecting lugs **40** and **41**, electrically and mechanically affixed respectively to end wall members **32** and **33**. As in the device of FIGURE 1, a suitable insulator shield such as metallic cylindrical member **43** terminating in an arc preventing ferrule **44** is interposed between electrodes **35–36** and insulator **31** to prevent the latter from becoming coated with sputtered or evaporated arc-electrode metal and be-

coming electrically short-circuited. The volume within chamber **30** is maintained at a pressure of less than 10^{-4} mm. of mercury and preferably less than 10^{-5} mm. of mercury, as is the device of FIGURE 1.

As is mentioned hereinbefore, one of the greatest problems in the commercial utilization of the basic concept of the vacuum switch has been in the provision of suitable arc-electrode materials. When used in inductive loads on alternating current circuits, a vacuum arc interrupter or vacuum gap device terminates the arc between the arc electrodes upon the occurrence of a first current zero. This is because when the alternating current cycle passes through zero the first time after the establishment of the alternating current arc, the voltage across the electrodes temporarily falls to zero, and the arc extinguishes. At this time the vaporized metallic particles from the electrodes which support the vacuum arc, immediately migrate to the nearest cold wall where they are condensed and deionized. Instantaneously the pressure within the device falls to a very low value and all available current carriers within the device vanish. Thus, when the voltage begins to build up for the next succeeding half cycle, the high dielectric strength of vacuum is interposed between the arc-electrodes and, in the absence of a second failure or exceeding of the rated voltage of the device, the arc is not restricken.

Two problems are in evidence. Firstly, it has been determined by others and is set forth in great detail in the patents of Lee and Cobine, No. 2,975,256 and of Lafferty, Nos. 2,975,255 and 3,016,436, that if the current zero is approached, a phenomenon known as "chopping" occurs and the current falls from a substantially high value to zero, inducing highly destructive transient currents within the circuit which can cause the breakdown of insulation in inductive circuit components, as for example transformers, motors, and generators. It was determined that such phenomena were due to vapor starvation and have been minimized or eliminated by the use of high vapor pressure materials as for example those set forth in the aforementioned U.S. Patents to Lafferty and Lee et al. for example. Such materials are non-refractory and have boiling points no higher than that of tin. Such use is often combined with portions of the electrodes which are refractory and may be outgassed to obtain the advantages of each type electrode material. Thus the refractory material does not erode badly, while the non-refractory, high vapor pressure material suppresses chopping.

In using high vapor pressure materials one encounters another difficulty attendant the use of vacuum gap devices with both fixed and movable gaps, namely that of maintaining a "hard" vacuum over a long duty cycle. In the operation of the vacuum switch and the vacuum gap, the arc stricken between the arc-electrodes melts the arc-electrodes at the footprints of the arc so that any gas entrapped in the arc-electrodes may be released therefrom and, when released, becomes ionized within the arc. Similarly, if low decomposition temperature gas-forming constituents such as for example, copper oxide are present within the arc-electode materials, these constituents may be decomposed by the temperature of the molten arc footpoint, to cause the release of gases which become ionized in the vacuum gap.

When the alternating current vacuum are passes through a current zero, even if there are ionizable gasses present, the arc is extinguished. In the event of the presence of ionizable gasses, however, the gap remains ionized and, when the next alternation of the applied inter-electrode voltage occurs and the voltage between the arc-electrodes builds up to a sufficient value, the arc is restricken and the vacuum gap has essentially failed to operate in its intended manner.

This problem is present not only if the entire electrode, as illustrated, is formed of a low melting point, high vapor pressure metal alloy. Some structures, as

for example as disclosed in U.S. Patents 3,239,635—Baude, and 3,244,843—Ross, utilize a combination of a refractory member and a low melting point, high vapor pressure member, both of which are subjected to the arc foot point at some portion of the arcing cycle. In such structures, the portion of the arc electrode that is non-refractory presents the same problem. Accordingly, it is imperative that the infusion of ionizable gasses into the vacuum gap due to the arcing action upon the electrodes be eliminated. In the past this has been done by the careful processing of the materials from which the vacuum arc-electrodes were fabricated by expensive, time-consuming, and tedious processes. Thus, for example, the prior art minimum for achievement of this objective has been determined to be at least a six-pass zone-refining process or the equivalent thereof.

Such a process requires that a large quantity of material, as for example copper, which is to be used in fabricating the arc-electrodes for vacuum gap devices be placed in a high temperature crucible, made for example from carbon or boron nitride, preferably in the form of a rod which may, for example, be 1 inch in diameter and 12 or 13 inches long. A molten zone which may, for example be one inch in longitudinal dimension, is then passed through the copper rod at a rate of, for example, 12 to 13 inches per hour. This takes about one hour. The process is then repeated, starting again with the molten zone at the same beginning end, for five more passages of the molten zone through the bar in the same direction. At the completion of this schedule, at least six to eight hours have been consumed in the processing of the material. In addition to the necessity of utilizing the passage of a molten zone through the copper rod a plurality of times special conditions must be maintained, as for example those set forth in Patent No. 3,234,351 to M. H. Hebb, which ensure the growth of large crystals of copper, thus minimizing the area of crystal interfaces at which gasses and gas-forming impurities tend to concentrate. The starting material for this process is generally of a very high purity, for example at least 99.96% pure in accord with A.S.T.M. standard B–170–47 and is nominally free of oxygen. One such starting material is "OFHC" copper, obtainable from American Metal Climax Inc., New York, New York, which has been analyzed as including approximately 99.995% copper, possessing approximately from 1 to 3 p.p.m. of oxygen.

While the aforementioned processes for the formation of electrode material to be utilized in vacuum arc devices of the vacuum switch and vacuum gap types is useful and is operative to produce practical electrodes and vacuum arc devices, it is expensive, time-consuming and requires the tying up of personnel and equipment for exceedingly long periods of time, thus limiting the amount of material that can be produced with any given facility. Accordingly it is imperative, if proper economy is to be effected in the manufacture of useful and effective vacuum arc devices that other means be found to fabricate vacuum arc electrodes.

I have found the principle gas which causes the aforementioned difficulties in normally processed materials for use as arc-electrodes in vacuum arc devices is oxygen. Oxygen is naturally present in large quantities in the environment in which practically all materials are refined and normally processed. Additionally oxygen is very reactive and readily forms oxides with normal electrode materials, as for example, copper. Oxygen, either in the gaseous form or in the form of metallic oxides, is almost invariably found to some degree in the most highly refined metals utilized in vacuum arc electrode processing. In particular, oxygen tends to accumulate at the grain boundaries and crystal interfaces in vacuum melted and zone-refined arc-electrodes.

Accordingly I have discovered that improved vacuum arc device arc-electrodes and vacuum arc devices may

be formed by the addition to the arc-electrode material, during processing, of small quantities of metals which have a very high affinity to oxygen and which form, with oxygen, highly stable refractory oxides which do not decompose at the temperature of the arc footpoint. Although there are several materials which satisfy these criteria and which may be considered suitable for this purpose such as the rare earths of the lanthanide series, for one reason or another each has some disadvantage. Beryllium on the other hand is the most effective remover of oxygen and does not otherwise detract from the operation of devices in accord with the invention by virtue of any of its other characteristics. It follows then, that the addition of small percentages of beryllium to copper arc-electrode material, for example, provides devices superior to any other combination. Additionally, I have found that the addition of small quantities of beryllium to conventional so-called high purity (OFHC or equivalent) copper having a purity of at least approximately 99.96 or purer copper and a nominal amount, for example, approximately 1 to 3 atomic parts per million of oxygen results in the formation of beryllium oxide, substantially all of which may be removed by suitable processing which is far simpler and less expensive than the aforementioned prior art fabricating processes.

More specifically I have found that when a small quantity as set forth hereinafter of material having a high affinity for oxygen and forming a high temperature refractive oxide therewith, principally beryllium, is added to a main constituent of a vacuum device arc-electrode, as for example, copper, and vacuum refined, for example, vacuum melted for ½ hour at 1080° C. at a pressure of 10^{-5} mm. Hg with directional cooling, a highly improved material is formed.

According to one preferred embodiment of the invention I prepare a quantity thereof in rod form which is subjected to a simple zone leveling process, which process is well known to those skilled in the art, and which may be found described in detail copiously in the literature as for example, in the book entitled Zone-Refining, by W. G. Pfann, published by John Wiley & Sons, New York, 1958, at pages 5 and 133 et seq. During zone leveling, the beryllium is intimately admixed with the copper during the passage of the molten zone therethrough. In general the characteristics of a metal or alloy which has been subjected to a zone leveling are well known to those skilled in the art, due to the known effects of the process upon the materials utilized. For this reason, and for simplicity of expression the electrode metal alloys used in practicing the present invention, when subjected to a zone leveling treatment will be referred to herein as "zone leveled" material. Generally such material and vacuum melted or conventional zone-refined material will be referred to herein as "vacuum refined" material.

Due to the segregation characteristic of beryllium in copper, during zone leveling the beryllium remains substantially uniformly distributed throughout the copper. The greatest portion of the oxide formed by the reaction of the beryllium with any oxygen present, either in the form of copper oxide or as free oxygen, while in the molten zone, floats to the outside surfaces of the molten zone and, upon freezing and cooling of the rod, may be seen as a cloudy surface contaminant. This beryllium oxide may readily be removed from the exterior surface of the zone leveled rod by etching in an acid etch, as for example, one generally comprising approximately one part hydrofluoric, three parts nitric and 10 parts acetic acid for a minute or less. Such etching removes the surface contamination which is the beryllium oxide and leaves the remaining ingot bright and free of oxide contaminants. Since the quantity of oxygen in the OFHC copper used initially is of the order of few atomic parts per million, substantially all of the beryllium added remains in the copper rod, approximately 5%, for example, of which is removed by cropping both ends thereof for purity sake. Due to the even distribution characteristic of the zone leveling process, the beryllium is substantially uniformly distributed throughout the copper in the form of a solid solution of the beryllium within the copper in one or more of the α, β, and γ phases or mixtures thereof, depending upon the temperature of the solidified ingot. The quantity of the beryllium added is, however, maintained below that concentration at which the first formed solid, upon cooling, contains any substantial amount of the δ phase which is the intermetallic compound $CuBe_3$. In the Be-Cu system this composition is the peritectic point occurring at approximately 11.5 wt. percent beryllium. The ingot also contains in a substantially uniform distribution a very small quantity of beryllium oxide which does not float to the surface.

Since zone leveling only requires one pass in each direction through the ingot, rather than the six passes in the same direction of the conventional zone-refining processes necessary for prior art device fabrications, approximately ⅔ of the cost and the work entailed in fabrication of arc-electrode material for vacuum arc devices as in the prior art is eliminated in accord with the present invention. Additionally, I have found that relatively impure copper may be rendered suitable for vacuum arc electrodes for use in certain low power applications in accord with the present invention by the addition thereto of relatively minor quantities of beryllium, so that the cost of the fabrication of such vacuum arc devices, in accord with the present invention, is drastically reduced from the cost of prior art fabrication methods.

In general, the affinity of a metal for oxygen is measured by the free energy of formation of the oxide. The more negative this value per atom of oxygen in the oxide, the greater the affinity of oxygen for the metal. The stability of the oxide so formed is measured by its dissociation temperature, when known. In the absence of a known dissociation temperature, the melting point and the boiling point are good criteria. In general, the higher the melting and boiling points, the more stable the oxide. Table I, below, lists these parameters for the oxides of copper, as a typical arc-electrode material, and the aforementioned materials.

	Free energy of formation at 1,080° C., Kcal	F/E/F per atom of O_2 Kcal.	Dissociation temp., ° C.	Boiling Point, ° C.	Melting Point ° C.
Oxide:					
CuO	−10	−10	1,026		
Cu_2O	−18	−18	1,800		
BeO	−110	−110		~3,900	2,500
La_2O_3	−336	−112		~2,400	2,315

From Table I it is apparent that both beryllium and lanthanum have at least approximately 10 times the affinity for oxygen that copper does at the melting point of copper. These materials rapidly associate with any oxygen present to form their own oxide. For optimum operation the oxygen affinitive metal used should have a free energy of formation per atom in the oxide of a more negative value than −100 Kcal. It is further evident that the oxides of these metal additives are highly stable and will not dissociate, even under arcing conditions. Reasons for the superiority of beryllium are that its vapor pressure is essentially the same as that of copper so that it does not adversely affect the characteristics of the copper-controlled arc. Additionally, upon arc-extinction, due to its low atomic weight, beryllium atoms are the first to condense

out of the vapor phase. Also, as compared with most rare earth metals, beryllium is more available and less expensive. Still another reason for the superiority of beryllium is that it is a monovalent element and forms only one oxide, BeO, which is known to be stable. Bivalent metals on the other hand, although having a stable oxide of the formula M_xO_y, where y is greater than one, may decompose to, or initially form, another less stable oxide, the characteristics of which are unknown or unpredictable.

Many other metals form stable oxides, but yet are unsuited or only marginal in the practice of the invention. Thus for example magnesium or any material with a lower boiling point may not be used because the vapor pressure of elemental magnesium and such other metals is too high to be consistent with vacuum gap devices and the inclusion of excess active metal is essential if all oxygen is to be removed. Similarly thorium forms a stable oxide but is unsuitable because the low work function of thorium makes its presence in excess elemental form highly undesirable in vacuum gap devices in addition to the fact that its stable oxide contains two oxygen atoms.

The amounts of the reducing metal which must be added to the major constituent of the vacuum arc electrode should be at least approximately one-tenth weight percent of the total and may vary depending upon the material. In general the maximum is no higher than the concentration which upon the phase diagram of the alloy results in formation during cooling, of a substantial amount of intermetallic compound in the first formed solid as temperature falls. Thus for example with copper as the main constituent, beryllium may be added in quantities ranging from approximately one-tenth to 11.5 percent by weight. Lanthanum, as an example of the lanthanide series of rare earth metals, may be added in quantities ranging from approximately 0.1 to less than 18% by weight. In general, as a practical matter the amount of oxygen reactive metal used is in the range of from approximately 0.01 weight percent to a quantity sufficient to leave, in the electrode after processing, an excess of from 0.1 to 10 weight percent of unoxidized metal.

Devices in accord with the present invention may be constructed by many alternative procedures. In one alternative, a simple alloy of the host arc-electrode material as, for example, so-called "tough pitch electrolytic" copper (99.9 pure) containing as much as several hundredths weight percent of oxygen, and a minor quantity of the oxygen removal constituent, as for example beryllium, may be prepared and cast in the desired shape, machined to the dimension required and assembled in the device as illustrated in FIGURE 1 or FIGURE 2 of the drawing. Upon assembly of the arc-electrodes in the device of FIGURE 1 or FIGURE 2, data as illustrated by FIGURES 3 and 4 are obtained. Although this embodiment of the invention is not elegant, due to the use of a low grade starting material and the lack of vacuum refining of the arc-electrode constituents, devices produced by this alternative are quite satisfactory for use in applications involving primarily low currents. For devices to be utilized at higher or very high (thousands of ampers) higher purity starting constituents and vacuum refining is desirable. As an alternative, therefore, the foregoing procedure may be practiced but the same mixing is done after high purity OFHC copper and SR grade beryllium have been separately zone refined by one or more passes.

In accord with other and preferred alternative procedures for forming devices in accord with the present invention, involving simple vacuum melting or zone-leveling of the alloy, devices adapted for high current operation are obtained and superior performance is achieved.

In accord with one preferred embodiment, simple vacuum melting with directional cooling for one to six times of the mixed constituents sufficient to insure reasonable admixture of the main constituent and the oxygen-reactive minor constituent under a good vacuum of, for example 10^{-4} mm. Hg and preferably 10^{-5} mm. Hg is utilized. Generally the process is of short duration and is conducted at the temperature of the melting point of the main constituent. A heat sink is available or a modified Bridgeman furnace is used to insure directional cooling. For example 3 pounds of OFHC copper and 2.4 oz. of SR grade beryllium obtainable from Pechinery Co., Paris, France, may be heated one or more times at temperature of 1100° C. for ½ hour and directionally cooled, washed in an acid etch of 1:3:10 parts of HF, HNO_3 and acetic acid to remove surface-collected beryllium oxide and washed in distilled water. Alternatively, mechanical means may be used to remove the surface-accumulated oxide. Although it is preferred to use OFHC grade copper as a starting material, "tough pitch electrolytic" copper may be used and satisfactory results obtained for devices for many uses, particularly for use at lower currents. Alternatively the same procedure as set forth above may be practiced with major and minor constituents each of which has been individually subjected to one or more "passes" of zone refining for purification purposes.

In accord with another preferred embodiment, high purity, nominally oxygen-free copper, as for example "OFHC" copper in the form of a rod of approximately one foot length and one inch diameter and weighing approximately 3½ pounds is placed in a boron nitride zone-refining "boat" type crucible and a quality of SR grade beryllium, which may for example be approximately 1% by weight in granular form, but is preferably zone refined with one or more zone refining passes, is disposed in the same crucible at the end at which zone-leveling begins. A movable coil of several turns, having a diameter sufficient to encompass the entire crucible boat containing the copper and the beryllium and having a longitudinal dimension such as to cause only approximately one inch of the copper to be molten at a given time, is connected to a source of radio frequency energy, as for example a one-half megacycle power RF oscillator. The movable coil is moved into position and energized to cause the beginning end of the copper rod and the beryllium present at that point to be heated to a temperature of approximately 1100° C. so as to melt and form a liquid zone approximately 1" long. The zone is gradually moved through the length of the copper rod at a rate of 12 to 13 inches per hour, during which time the beryllium has an opportunity, because of its segregation coefficient in copper, to remain in the molten phase and collect the oxygen within the newly molten copper. As this oxygen is collected, beryllium oxide is formed and floats to the external surface of the rod. After cooling the oxide may readily be removed by an acid bright etch, as for example a mixture of one part HF, three parts HNO_3 and ten parts acetic acid, thus effectively removing substantially all of the oxygen from the copper bar but retaining substantially all of the added beryllium in the bar. The zone continually passes through the bar and, upon the completion of the pass, the direction of passage is reversed and run back to the point of beginning at the same rate.

This zone leveling evenly distributes the beryllium and any minute residual entrapped beryllium oxide evenly throughout the bar. Because the remaining beryllium oxide is evenly distributed throughout the copper bar and is of such a low concentration, it cannot be noticed in the operation of the device. Similarly the minor constituents of beryllium, as compounds and in alloy form is present, but enhances rather than detracts from device characteristics. As with vacuum melted arc-electrodes, zone leveled arc-electrodes, particularly those to be used at lower currents may also be made using "tough pitch" electrolytic copper rather than OFHC or equivalent grade as a starting material.

After cooling and cropping of approximately ½" from each end of the single pass zone-refined bar, the surface coating of oxide is removed by a suitable process. For

example the bar may be washed in an etch containing approximately one part hydrofluoric and 3 parts nitric acid and 10 parts acetic acid for approximately 1 minute to remove the surface concentration of beryllium oxide. The bar is then rinsed in distilled water and dried, and is further cast in vacuo by well known techniques to form the proper size and shape electrodes as illustrated in FIGURES 1 and 2 of the drawing. Upon formation of the electrodes as in FIGURES 1 and 2 the electrodes are assembled within the devices of FIGURES 1 and 2 which are then ready for operation.

In accord with another embodiment of the invention a beryllium-copper alloy, as for example Berylco No. 10, obtainable from the Beryllium Corporation, P.O. Box 429, Hazleton, Pennsylvania and containing 0.55 wt. percent of beryllium, the remainder copper with a trace of cobalt, may be zone leveled or multiple pass zone refined or vacuum melted with directional cooling and the removal of beryllium oxide as described hereinbefore with satisfactory results.

Devices, as illustrated in FIGURES 1 and 2 of the drawing, constructed in accord with the invention exhibit essentially the same or improved desirable initial electrical characteristics as do the devices of the prior art utilizing copper electrodes only, which copper is, previous to formation of the electrodes, subjected to a conventional six pass zone-refining purification process to remove sorbed oxygen and oxygen-containing constituents therefrom. Additionally devices in accord with the present invention maintain these desirable initial conditions for a longer period of time due to the ability of the beryllium present in the electrodes to maintain the volume free of evolved oxygen and retaining the hard vacuum essential to vacuum gap operation.

The invention is not limited to the use of copper electrodes so formed. Silver may be substituted for copper in any portion. Additionally, in many instances such devices utilize arc-electrodes of copper and other additives to improve on "chopping," welding and other undesirable characteristics often found in vacuum gap and vacuum switch devices as is set forth in the aforementioned Lee et al. and Lafferty patents.

It is within the intended scope of the present invention that the copper or other material which constitutes the main constituent of vacuum gap eletcrodes as described therein as well as the materials which constitute the minor constituents thereof, be vacuum purified of oxygen by this procedure before combining with other constituents, thus effecting the same benefits as if performed in the fabrication of devices utilizing copper electrodes only. Other metal arc-electrode constituents may be similarly prepared. Thus for example the devices set forth in the aforementioned Lee et al. patent may be likewise prepared.

FIGURE 3 of the drawing illustrates, in graphical form, the recovery strength of devices in accord with FIGURE 2 of the drawing after peak arcing currents of 250 A. indicating the substantial equivalency between certain characteristics of devices constructed in accord with the present invention utilizing beryllium-copper electrodes as compared with six pass zone-refined copper electrodes. In FIGURE 3, the voltage held off by the vacuum gap of the device of FIGURE 2 as a function of time is plotted for delayed voltage pulses applied after arcing of a device utilizing conventional six-pass zone-refined copper electrodes, illustrated by the hollow round dots as compared with a device utilizing copper electrodes containing less than 1% minor constituent of beryllium in accord with the invention, illustrated by the solid square dots. As may be seen from FIGURE 3 there is substantially no difference between the two characteristics, for the duty life tested.

FIGURE 4 of the drawing shows data on the impulse breakdown voltage, as a function of gap length, for a vacuum gap device utilizing conventional six-pass zone-refined copper electrodes, illustrated by the hollow circular dots and for a vacuum gap device in accord with the invention utilizing copper electrodes containing less than 1% by weight of beryllium, illustrated by the solid square dots. As illustrated by the data of FIGURE 4, the tested duty life impulse breakdown voltage of devices constructed in accord with the present invention utilizing copper electrodes having a minor constituent of beryllium (less than 1% by weight) are substantially the same as the same characteristics of conventional vacuum gap devices utilizing conventional six pass zone-refined copper electrodes

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A vacuum gap electric discharge device comprising:
(a) a hermetically sealed envelope evacuated to a pressure of 10^{-4} mm. of Hg or less and including at least a portion thereof comprising a high voltage insulator
(b) a plurality of electrodes including at least a pair of primary arc-electrodes disposed in insulating relationship within said envelope and defining therebetween a breakdown gap,
(b_1) at least two of said electrodes each having at least a portion thereof adapted to present an arcing surface to sustain a footpoint of an electric arc,
(b_2) at least said portions of said electrodes comprising a non-refractory major constituent having an electrical conducting characteristic suitable for arc-electrode use and high vapor pressure, and a minor constituent selected from the groups consisting of beryllium and the lanthanide series rare earths having a high affinity for oxygen and forming therewith a high temperature stable oxide to remove and retain from said major constituent oxygen contained therein;
(b_3) said minor constituent of said portion of said arc-electrodes being present in a quantity of approximately 0.1 by weight to a maximum value which corresponds to a composition on the alloy phase diagram at which cooling of the liquid results in the formation of a first-formed solid phase and containing no substantial quantity of intermetallic compounds; and
(c) means for striking a conducting electric arc between said arc-electrodes.

2. The vacuum gap electric discharge device of claim 1 wherein the minor constituent is beryllium within the range of approximately 0.1 to 11.5 weight percent of said portions.

3. The vacuum gap electric discharge device of claim 1 wherein the major constituent is copper.

4. A vacuum gap electric discharge comprising:
(a) a hermetically sealed envelope evacuated to a pressure of 10^{-4} mm. Hg or less and including at least a portion thereof comprising a high voltage insulator;
(b) a pair of primary arc-electrodes disposed in insulating relationship within said envelope and defining therebetween a breakdown gap, said arc-electrodes each having at least a portion thereof adapted to present an arcing surface to sustain a footpoint of high current electric arc,
(b_1) at least said portions of said electrodes comprising oxygen free vacuum refined material having a major non-refractory constituent having an electrical conductivity suitable for arc-electrode use and high vapor pressure, and a minor constituent selected from the group consisting of beryllium and the lanthanide series rare earths having a high affinity for oxygen and forming therewith an oxide which is stable at the temperature of the molten electrode at the arc footpoint sufficient to remove and re-

tain from said major constituent prior to device assembly any oxygen contained therein,

(b_2) said minor constituent of said portion of each of said arc-electrode being present in a quantity of approximately 0.1 weight percent of the total weight of said portions to a maximum value represented by a composition on the phase diagram of the alloy at which cooling of the liquid results in the formation of a first-formed solid phase containing no substantial quantity of intermetallic compound as excess minor constituent, and

(c) means for establishing a conducting electric arc between said arc electrodes.

5. The vacuum gap electric discharge device of claim **4** wherein the minor constituent is beryllium in the range of approximately 0.1 to 11.5 weight percent of said portions.

6. The vacuum gap electric discharge device of claim **5** wherein the major constituent is copper.

7. The vacuum gap electric discharge device of claim **5** wherein beryllium is present in a concentration of at least approximately one weight percent.

8. The vacuum gap electric discharge device of claim **5** wherein beryllium is present in a concentration of at least approximately 5 weight percent.

9. The vacuum gap arc electric discharge device of claim **4** wherein said minor constituent is lanthanum in a concentration of approximately 0.1 to 18 weight percent.

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