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METHOD OF MAKING A TUNGSTEN-NICKEL ALLOY FILAMENT

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Fig. 1.

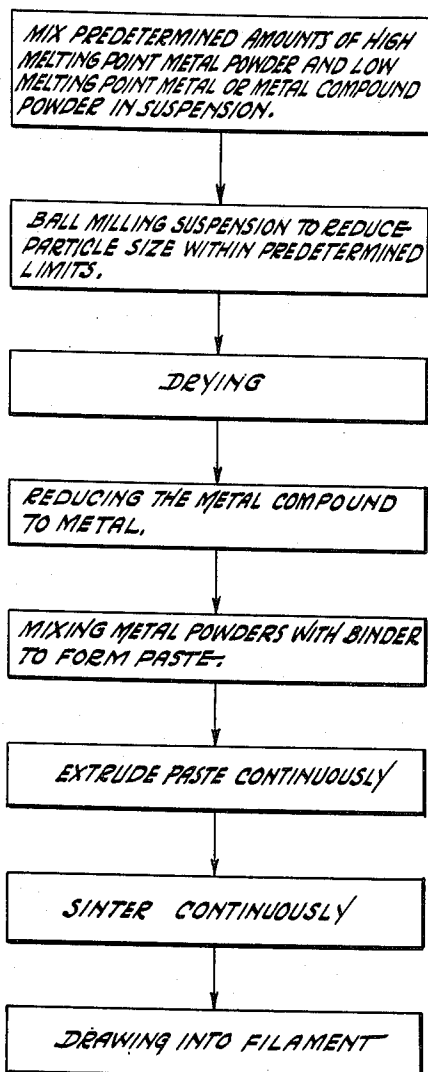
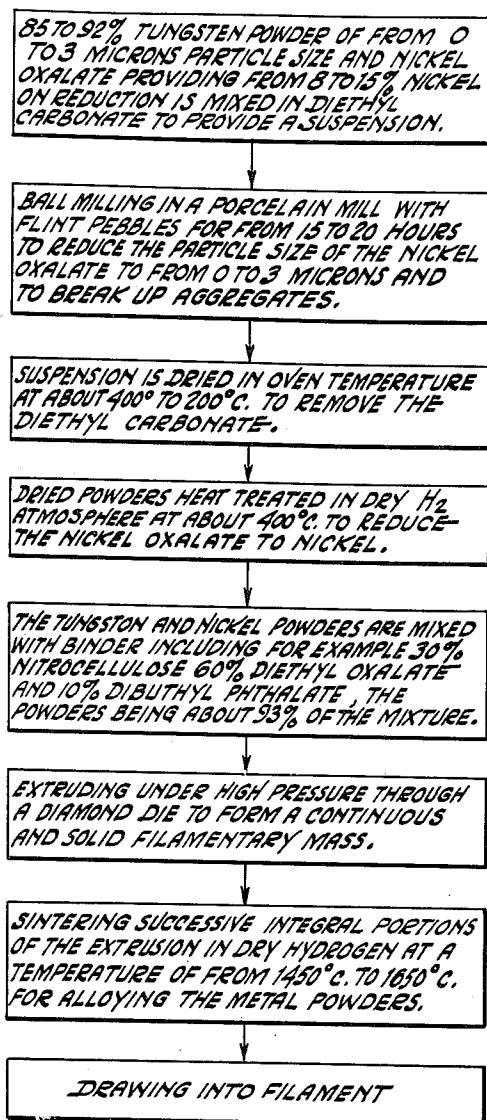


Fig. 2.



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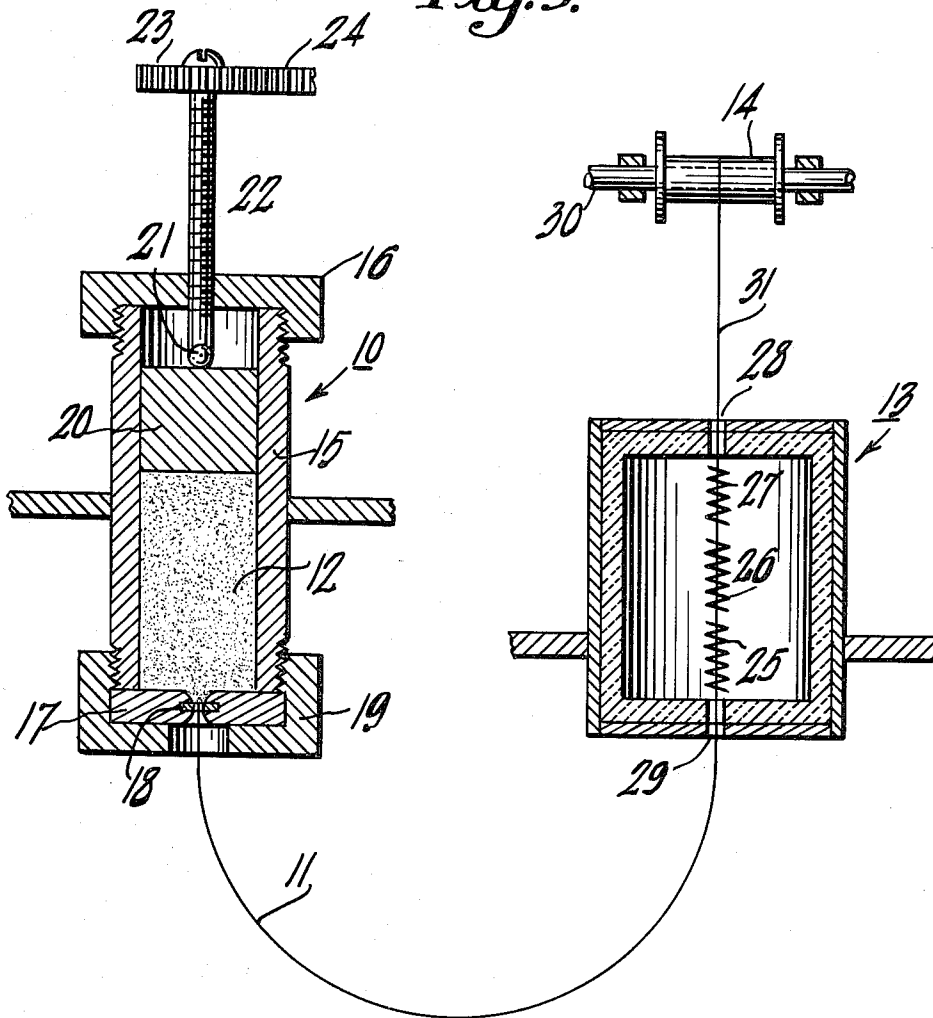
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Fig. 3.



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METHOD OF MAKING A TUNGSTEN-NICKEL ALLOY FILAMENT

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4 Claims. (Cl. 75—207)

The present invention relates to an alloy composed of metals or groups of metals having differing melting points, particularly useful as the base for a directly heated electron emitter having high hot strength, and to a method of making such alloy.

Some types of electron emitters comprise a filamentary or ribbon metal base coated with oxides of alkaline earth metals. The base is usually composed of a nickel alloy, but where high hot strength is required this material is not satisfactory. In such cases metals such as tungsten or metallic alloys must be used having high hot strength. The preparation of a filament from this material involves compressing powders of the metal or metals used to form bars of predetermined length, followed by sintering and rolling or swaging of the bars, and subsequently drawing through dies to the required size for a cathode base.

Several limitations characterize this process. It is necessarily discontinuous in operation and constitutes a repetition of work cycles, each cycle involving a separate and distinct work piece. Thus, each cycle of the prior process includes a series of operations comprising forming bars of predetermined length, sintering and swaging the bars, and drawing to required size.

It has not been considered feasible heretofore to employ a continuous method utilizing powder metallurgy for making an alloy filament. The reason for this is that a continuous method requires the material to be self supporting while the process is being practiced, and such self support has been absent both during transit of the material between stations of the process and during the heating step. At the heating station it is desirable that the material be free from contact with the apparatus or any supporting medium and the only feasible manner of accomplishing this result is to suspend the material at this point thus allowing it to be free from such contact. This calls for a sufficiently high hot strength of the material during formation to prevent stretching or breakage. This requirement for high hot strength has heretofore made it impractical to produce an alloy filament by a continuous extrusion or powder metallurgy process.

The base material of a filamentary or ribbon type of oxide coated cathode should satisfy certain requirements in use. For example, the material should possess a sufficiently high hot strength to avoid stretching or other deformation thereof when the cathode is operated at relatively high temperatures and suspended under an appreciably high tension. Moreover, the erratic emission from the cathode that occurs as a consequence of the use of pure tungsten as the base material should be suitably controlled. One way of controlling this erratic emission is to alloy the tungsten with a metal having a more stable effect on emission, such as nickel, for example. However, nickel has a much lower melting point than tungsten and, consequently, its addition to tungsten in excess of 15 to 20% appreciably reduces the hot strength of the resultant alloy, to such a point as to impair its use as the base for a cathode of superior strength and to render

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a continuous powder metallurgy process for making the alloy impracticable.

A further objection to the prior discontinuous process of making a ribbon or filamentary body resides in the critical controls required for carrying out the process. Thus, a plurality of annealing operations at critically controlled temperatures are necessary for maintaining the work pieces ductile.

Accordingly, it is the object of the invention to make an alloy of metals or groups of metals having widely differing melting points by a continuous powder metallurgy process.

A further object is to provide a continuous method for making a ribbon or filamentary base for a cathode that will contribute to stable emission of the cathode and preserve the hot strength required of the cathode.

Another object is to provide a method for making a cathode base that is characterized by fewer critical controls than prior methods.

A further object is to provide a continuous method of making a cathode base of a material including a relatively high melting point metal for required hot strength of the cathode, and a lower melting point metal for required stable emission of the cathode.

Another object is to provide an alloy of a relatively high melting point metal or group of metals and a relatively low melting point metal or group of metals for a cathode base that will contribute to improved emission of the cathode in which it is used and will possess the required hot strength for permitting a continuous process to be followed in its fabrication and for permitting use at relatively high temperatures at high tension without stretching or otherwise becoming deformed.

According to one aspect of the invention a continuous powder metallurgy process is employed for making a base for a cathode that will contribute more stability of emission than tungsten alone. The alloy includes a predetermined relative amount of a high melting point metal such as tungsten or group of metals such as tungsten and molybdenum and a metal having a much lower melting point such as nickel or group of metals such as nickel and copper. The amount of the first named metal or metals is such as to preserve the required degree of hot strength of the base during manufacture and during use in a cathode, the amount of the second named metal or metals being such as to contribute to an appreciable stabilization of emission.

Another aspect of the invention concerns the size of the metal powder particles employed in practicing my novel method.

I have found that relatively small sized particles impart desired tensile strength to an extrusion including the particles and improves the hot strength of the resultant alloy to thereby facilitate the use of a continuous process and render the alloy suitable for a cathode base.

Further objects and advantages of the invention will become apparent as the present description proceeds.

Referring to the drawing:

Figure 1 shows a flow sheet indicating generally the character and order of the steps employed in the practice of my novel method;

Figure 2 shows a flow sheet indicating in more detail the steps of a preferred method according to the invention; and

Figure 3 is an elevational view partly schematic and partly in cross-section, showing one type of apparatus that may be employed in practicing the novel method of the invention.

According to one way of practicing my novel method as shown in Figure 1, powders of a relatively high melting point metal and of a relatively low melting point met-

al or compound of the latter metal are mixed in a suspension in predetermined relative amounts and ball milled to reduce the particle size of the powders to within a predetermined size range. The suspension is then dried, and where the powders include the powder of a metal compound, they are subjected to a reducing step to reduce the metal compound to the metal state. The metal particles are then mixed with a binder to provide a paste which is then continuously extruded to form a continuous extrusion which may be of filamentary form. The extrusion is then sintered continuously at a sintering station where it is supported in a pendent fashion for alloying the powdered particles. The sintered and alloyed body is then cooled and drawn through a suitable die to more critical dimensions required of the finished product such as a filament or ribbon.

The particular particle size of the metal powders resulting from the ball milling step and the critical relative amounts of the powders of the high and low melting point metals, result in a material having the necessary tensile strength for unimpaired transit from the extrusion station to the sintering station as well as the required hot strength for preserving its shape during the sintering step without stretching or rupturing.

More specifically as shown in Fig. 2, pure tungsten powder having a particle size range of from 0 to 3 microns in diameter and preferably with particle size fractions at from 1 to 2 microns, is mixed with pure nickel oxalate in predetermined relative amounts necessary, on reduction in hydrogen, to give from 8 to 15% nickel and 92-85% tungsten by weight. The mixed powders are ball-milled in a porcelain mill with flint pebbles and in the presence of diethyl carbonate for from 15 to 20 hours to reduce the particle size of the nickel oxalate and to break up aggregates. The fluid mixture is then dried in an oven at a temperature of from 100° to 120° C. to remove the diethyl carbonate and the fine powders resulting are heat treated in a silica boat in a silica tube electric muffle furnace in a dry hydrogen atmosphere at approximately 400° C. The mixture of tungsten and nickel powders is then thoroughly mixed with approximately 7% by weight of a binder composed by weight of 30% nitrocellulose of one half second viscosity, 60% diethyl oxalate and 10% dibutyl phthalate.

The resultant mixture is then extruded under relatively high pressure through a suitable forming tool such as a diamond die. The pressure referred to forms the paste into a solid filamentary mass that is capable of movement to a sintering station without losing its form.

The extrusion prior to sintering may be supported in a hanging manner from a winding head and in the sintering station is out of contact with adjacent parts of the apparatus employed in my method to prevent alloying with or contamination of the extrusion by the material of such apparatus. Successive integral portions of the extrusion are fed by the winding head to the sintering station to provide a continuous sintered alloy body of indefinite length.

The temperature employed at the sintering station in this example is from 1450° C. to 1650° C. This is substantially below the melting point of tungsten which is approximately 3370° C. The temperature range referred to, however, begins at the melting point of nickel which is 1450° C. and may rise slightly thereover as indicated. During the sintering step the extrusion is disposed in an atmosphere of dry hydrogen.

The sintered alloy body is then drawn after cooling through a die to provide a finished product having desired dimensions.

Several explanations are available for the fact that my novel method results in an extrusion that is self supporting during travel from the extrusion station to the sintering station and during the sintering step. For example, limitation of the particle size to a range from 0 or less than the smallest measurable size to 3 microns

results in a close and dense packing of the powders at the extrusion station to provide a solid filamentary mass of relatively high tensile strength. This strength is sufficient to enable the extrusion to withstand the forces applied thereto in traveling from the extrusion station to the sintering station without deformation. Moreover, the critical range of relative amounts of nickel and tungsten powders in the extrusion, and the employment of a temperature that is substantially below the melting temperature of tungsten at the sintering station, permits the sintering step to be carried out with the extrusion suspended without elongation or other deformation thereof. While the hot strength of the filament at the sintering position is greatly reduced by the addition of nickel thereto, a limitation of the relative amount of tungsten to from 85% to 92% of the powder mixture has been found to preserve sufficiently the hot strength of the filament at this point to permit sintering thereof while supported without appreciable deformation thereof.

At the operating temperature of a filamentary cathode, which is about 800° C. tungsten has a tensile strength of about 225,000 pounds per square inch, while nickel alloys as ordinarily used have a tensile strength of approximately 30,000 pounds per square inch. A filament made in accordance with my method has a hot tensile strength considerably higher than that of the nickel alloys mentioned and that approximates the tensile strength of tungsten. Thus an alloy made in accordance with my method and including about 92% tungsten and about 8% nickel has a tensile strength at 800° C. of about 150,000 pounds per square inch and an alloy of about 12% nickel and about 88% tungsten made according to my method has a tensile strength of about 100,000 pounds per square inch. For purposes of use in a filamentary or ribbon type cathode suspended under an appreciable tension, my alloy is therefore particularly advantageous in that not only does it possess the hot strength necessary for a tensioned suspension, but at the same time in conjunction with the oxide coating develops and sustains the necessary stable emitting characteristics.

My novel method is particularly adapted for continuous operation in view of the fact that the extrusion initially made thereby is resistant to deformation during transit and during the subsequent sintering step. Consequently a continuous extrusion can be formed from a renewable reservoir of the paste including the metal powders referred to and caused to travel continuously through several stations including the sintering station, the finished filament or ribbon being subsequently received by a storage means such as a reel or spool. The finished product has high ductility and in view of sintering in hydrogen has a clean and polished metallic surface. An indefinite length of the finished material can be obtained as a consequence of my novel method since the process continues so long as the extrusion paste is fed to the extrusion die. The continuous character of my method moreover particularly adapts it for mechanization for securing increased output and economy.

An important advantage resulting from the continuous character of my method is that a reduced number of critical controls is required for its practice. For example, once the rate and pressure at which the material is extruded and the temperature of the sintering station have been fixed, my method requires no subsequent adjustment in view of the continuity of these fixed conditions during the time that my method is practiced. A further important result of my method is that the product produced thereby is more uniform than that made by prior discontinuous methods, and consequently cathodes made from my novel alloy are generally more uniform in performance.

According to another way of practicing my method, multiple alloys, such as tungsten, nickel and copper may be made. Powders of tungsten, nickel and copper are processed as indicated before herein to provide a particle

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size lying within the range of from 0 to 3 microns. The same proportion of tungsten employed in the foregoing example is used in this instance, the remaining 8 to 15% comprising nickel and copper powders, the amount of nickel being greater than copper, the nickel being preferably three times that of copper.

The metal particles referred to are mixed and added to a paste having the composition previously described and thoroughly mixed therewith. The resultant product is then extruded under relatively high pressure, sintered and drawn under the conditions referred to in the prior example.

While my method and resultant alloy have been described in connection with tungsten, nickel and copper, it is not to be regarded as limited to these metals. My method is useful in forming an alloy of any two metals or groups of metals, one of which has an appreciably separated melting point from the others. Thus the high melting point metal or group of metals required for the practice of my invention may comprise molybdenum, or any other alloying metal having a relatively high melting point or mixtures of same, instead of tungsten. And instead of nickel or copper I may use a suitable metal or combination of metals having a relatively low melting point.

While my method is thus subject to variation in respect of the metals involved, its requirement for a separation in the melting points of at least two metals or groups of metals employed cannot be ignored. This is for the reason that the support of the extrusion which is necessary for my continuous method is dependent on the freedom from melting at the sintering station of at least one of the metals or group of metals used in forming the alloy. If all the metals employed should melt during the sintering step the extruded body would lack the required tensile strength for self-support and as a consequence would stretch and break when supported as required by the practice of my method. Therefore, a metal or group of metals having an appreciably high melting point should be used within the limits specified in connection with a metal or group of metals within the limits specified, having a lower melting point, in the practice of my method so that the tensile strength imparted to the extrusion by the higher melting point metal will persist during the sintering step.

The resultant alloy produced by my novel continuous powder metallurgy method includes small amounts of carbon resulting from the decomposition of the paste during the heat treatment referred to. Thus, I have found that my alloy contains from about 0.10 to 2% by weight of carbon. This material in the amounts present contributes the advantage of aiding the emission of a cathode in which my novel alloy is used as the base. In a similar manner other reducing agents, such as magnesium, titanium, silicon or aluminum, may be added directly in small amounts as indicated for improving emission characteristics, if necessary.

One way in which the method of the invention may be practiced is shown in Figure 3. The apparatus shown includes a gun 10 adapted to form an extrusion 11 from a paste 12. The paste includes nickel and tungsten powders of a particle size and in the relative amounts indicated before herein, and a carbonaceous binder held in suspension in a volatile medium.

The apparatus also includes a furnace 13 to which the extrusion is fed, for sintering the metal components of the extrusion and for driving off the volatile medium referred to, to provide an alloy filament comprising tungsten, nickel and carbon. The alloy filament is collected by a reel 14.

Considering the structure referred to in more detail, the gun includes a cylinder 15 closed at one end by a cap 16 and having at the other end a die member 17 including a diamond die 18. The die member 17 is held in position by means of a cap 19 screwed to the

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cylinder 15. A piston 20 fitting snugly in cylinder 15 is adapted to transmit pressure to the paste 12 to force the paste through the diamond die 18 to form the extrusion 11. In one example, the die opening was 0.01 inch to provide an extrusion having a diameter of 0.01 inch. Bearing against the end of piston 20 remote from the paste 12, is a ball bearing 21 against which one end of a shaft 22 is adapted to apply pressure. The shaft referred to is screw threaded through the cap 16 for axial movement against the bearing 21 and piston 20. At the end of shaft 22 remote from the bearing 21, is fixed a spur gear 23 which is driven by a spur gear 24 forming part of an automatic power transfer system, not shown. In one example, the power transfer system was adapted to turn the spur gear 23 one and one-quarter revolution per hour to provide an extrusion flow from the die member 17 of 25 feet per hour.

The extrusion emitted by the die member 17 has sufficient tensile strength to render it self-supporting during transit thereof to and through the furnace 13. Consequently the extrusion is free from contact with any portion of the furnace referred to.

The furnace 13 includes preferably three heating elements 25, 26, 27, which may be connected to a suitable power source not shown, for providing a desired gradient in heat application to the extrusion 11 passing therethrough. The heating elements are preferably in the form of aligned coils defining a passageway in line with openings 28, 29 in the furnace, through which the extrusion is adapted to pass.

The reel 14 is disposed above the furnace 13 and in line with the passageway referred to through the furnace. The reel includes a shaft 30 which is connected to a power source, not shown, for turning the reel to take up the sintered alloy filament 31. In addition means, not shown, may be provided for moving the reel rectilinearly to maintain the filament 31 in line with the passageway through the furnace 13.

It will be noted that the arrangement shown of the gun 10 and the furnace 13 results in the formation of a looped extrusion 11. This is advantageous since slight variations in the speed of extrusions fed by the die member 17 and the speed of take-up by the reel 14, may be absorbed by slight contractions or expansions of the loop.

It will be noted from the foregoing that the apparatus described is adapted to form a continuous filament of indefinite length. This feature particularly distinguishes the invention from prior practices which involve first forming a slug and then drawing the slug to desired filament form. Not only are such prior practices discontinuous, but they are characterized by frequent slug breakages in drawing, resulting in impaired economy.

It is apparent from the foregoing that my invention is capable of many modifications without departing from the spirit of the invention, and it is desired to include such modifications within the scope of the appended claims.

I claim:

1. Method of making an alloy of tungsten and nickel, comprising mixing in paste form powders of tungsten and nickel having a particle size of up to three microns in diameter and in the relative amounts of from 8% to 15% nickel and from 92% to 85% tungsten, continuously extruding said paste to desired filamentary shape to form a moving extrusion, supporting the moving extrusion for suspension only from both ends thereof, and heating successive portions of the moving extrusion so supported and wholly free from contact with contaminating materials in a non-oxidizing atmosphere to a temperature of from 1450° C. to 1650° C. to sinter the metal particles in said powders to form a tungsten-nickel alloy filament, said moving extrusion having a

hot strength sufficient for preventing appreciable elongation thereof when subjected to said temperature.

2. A continuous method of making a tungsten-nickel alloy filament containing carbon by a powder metallurgy process, comprising mixing in a carbonaceous vehicle powders of tungsten and nickel having a particle size up to three microns in diameter and in relative amounts by weight of from 8% to 15% nickel and from 92% to 85% tungsten, continually extruding from a predetermined location the mixture of said powders and vehicle to form a moving extrusion of predetermined cross-section supported at one end at said predetermined location, supporting the other end of said moving extrusion at another location spaced from said predetermined location for suspending vertically a portion of said moving extrusion at said another location, said moving extrusion being supported only from said two ends thereof, and heating said portion of the moving extrusion so supported and wholly free from contact with contaminating materials in a non-oxidizing atmosphere to a temperature of from 1450° C. to 1650° C. to drive off volatile components of said vehicle and to sinter the metal particles of said powders to form a tungsten-nickel alloy filament without deforming said predetermined cross-section of said moving extrusion.

3. Method of making a base for a filamentary cathode having increased hot strength and contributing to improved emission from the cathode, said method comprising the steps of mixing powders of tungsten and nickel in paste form and in the relative amounts by weight of from 8 to 12% nickel and from 92 to 88% tungsten and wherein said powders have a particle size of up to three microns in diameter, continuously extruding said paste to filamentary shape to form a moving extrusion having two opposite ends, supporting said moving extrusion for suspension at both of said ends only, and melting said nickel particles in successive portions of said extrusion while so suspended and wholly free from contact with contaminating materials in a non-oxidizing atmosphere, for forming a tungsten-nickel alloy filament having a tensile strength at 800° C. of at least about 100,000 pounds per square inch.

4. Method of making a filamentary cathode base having increased hot strength and contributing to increased electron emission from a cathode in which it is used,

said method comprising extruding downwardly from an extrusion gun a paste including tungsten and nickel particles up to three microns in diameter and in amounts by weight of from 85 to 92% tungsten and from 8 to 15% nickel, whereby a moving extrusion supported at one end by said gun and extending downwardly from said paste is formed, supporting the other end of said moving extrusion remote from said gun at a location at least as high as the lower end of said gun, whereby said extrusion defines a loop supported solely at said ends thereof, and melting said nickel particles in successive portions of said moving extrusion in said loop and adjacent said location and wholly from contact with contaminating materials in a non-oxidizing atmosphere to form a tungsten-nickel alloy filament, whereby one portion of said loop comprising said alloy is supported independently of the non-alloyed portion of said loop, for preserving said extrusion from rupture.

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