UNITED STATES PATENT OFFICE.

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MANUFACTURE OF REFRACTORY CONDUCTORS.

1,026,343. Specification of Letters Patent. Patented May 14, 1912.

No Drawing. Application filed June 7, 1907. Serial No. 377,781.

To all whom it may concern:

Be it known that I, WILLIAM D. COOLIDGE, a citizen of the United States, residing at Schenectady, county of Schenectady, State of New York, have invented certain new and useful Improvements in the Manufacture of Refractory Conductors, of which the following is a specification.

This invention relates to the production of refractory electrical conductors suitable for use in incandescent lamps, electric furnaces, and other apparatus.

My present application is a continuation in part of applications made by me as follows: Serial Nos. 316,005, and 316,006, metal filaments, filed May 9, 1906; Serial Nos. 328,724 and 395,422, graphite filaments, filed August 1, 1906 and October 1, 1907, respectively; Serial No. 328,726, refractory conductors, filed August 1, 1906.

My invention comprises a process whereby refractory material, even though nonductile, may be shaped into wires, plates, rods, or other forms, and then consolidated into coherent conductors capable of converting electrical energy into light at enormously high temperatures.

According to my invention, an element, alloy, compound, or mixture is incorporated with a metallic binder, and the product so obtained is squirted or otherwise shaped into rods or filaments and then treated to drive out the easily vaporizable auxiliary metal or binder and to consolidate and sinter together the refractory residue.

My process is applicable to a great variety of refractory metals and materials, such, for instance, as tungsten, molybdenum, boron, zirconium, tantalum, titanium, graphite, or to compounds or alloys of any of these, or of other materials of the same general refractory nature. As a binder I use metallic material capable of being impregnated with the material from which the conductors are to be produced and also vaporizable by heat treatment at a suitable temperature. Binders such as that which I have hereinafter described do not, generally speaking, appear to chemically combine with the material with which they are impregnated, and, consequently, the process of manufacture is not limited to the materials above mentioned. The binder which I have described is, furthermore, of such a nature that part of it will vaporize at relatively low temperatures and part at higher temperatures, so that elimination of the binder may go on progressively or fractionally. In general the auxiliary metal or binder serves to give the body ductility and strength, and in some cases to increase its electrical conductivity, and is retained only until the body has been worked or formed into the desired shape. It is then driven out by heat treatment and leaves behind a refractory coherent wire or rod suitable for use in lamps. One binding material which I may use is an alloy containing cadmium, mercury, and bismuth. This alloy may have the following proportions:—cadmium 42%, mercury 53%, and bismuth 5%.

In order that my invention may be easily practised, I have hereinafter described the process as applied to the metal tungsten, but this specific application is to be regarded as only typical and as showing but one of numerous applications.

Tungsten suitable for use according to my process may be made by reduction of tungsten trioxid with hydrogen according to the general process well known to chemists.

To compound the binder for use with tungsten or other refractory powder, I melt together the bismuth, cadmium, and mercury in the proportions above mentioned. I find that the mixture melts considerably lower than the temperature at which cadmium oxidizes in air, and I find that the alloy is smooth, and when partially cooled is plastic and may be readily impregnated with the fine particles of the tungsten powder by simply rubbing the two together with a pestle in a chemist's mortar. The tungsten may be added to the extent of 30 to 40 per cent. by weight of the final mixture. I call the product a mixture because I do not at present believe that the tungsten alloys or combines in any way with the material of the binder. The mixture is ductile and pliable and can be readily rolled or worked by any of the well known metal working processes.

To obtain wires suitable for the construction of incandescent lamp filaments, I squirt the plastic mixture above mentioned through a diamond die at a temperature of 100 to 150° C. The material comes out as a

smooth, silver-white wire, very pliable and tough. The mixture is suitable for squirting in sizes varying from large rods down to wires having a diameter of one mill or even less. The ductile wire is cut to length and bent in loops having the shape of the lamp filament. The loops may then be fired in bunches in an evacuated tube heated with a gas flame. During this baking operation, most of the mercury and some of the cadmium come out, but most of the bismuth and preferably some of the cadmium stay behind with the tungsten. The evacuated baking tube may consist of glass, and in that case offers the advantage that the treatment is in a sense fool-proof for the reason that the glass softens at such a low temperature that it cannot readily be heated high enough to drive the bismuth from the wires. This treatment of firing the wires in a heated tube is a step which may conveniently be employed as a method of removing part of the binder before the conductors are heated with current as hereinafter set forth; but it is not claimed by me, being in itself, I believe, the invention of Howard I. Wood. The baked filament loops above described are next suspended in treating bottles and heated with current to drive out the remainder of the binder. Each loop can be suspended in the treating bottle between metal clamps. The treating bottle should be evacuated with a good mechanical pump and should be maintained dry by the use of an absorbing agent, such as phosphorous pent-oxid. I prefer to have this drying agent in close proximity to the filament, as in a small dish placed immediately below the filament during treatment. The treatment of the filament loop is carried out by passing a low current through the loop for ten or fifteen seconds and then a higher current for fifteen to thirty seconds or even for a minute. The low current heats the loop sufficiently to drive out the remaining cadmium and bismuth. The high current sinters the residue together and shrinks the loop into a compact, homogeneous wire having a bright metallic surface. The sintering current need not be higher than the normal running current of the filament, though if desired it may be made considerably higher, thereby shrinking the filament more rapidly. The sintered loop is strong enough for commercial use in incandescent lamps and can be operated in lamps at a very high efficiency.

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

1. The method for the manufacture of articles of refractory metal which consists in incorporating together to form a coherent workable composition refractory metal and other metals adapted to be expelled by heat at substantially different temperatures, forming the article desired from the composition, and heating to eliminate said other metals from the article successively and convert it into a coherent refractory one.

2. The process for manufacturing refractory articles which consists in incorporating powdered material in a cadmium alloy, shaping and manipulating the resulting material as desired, and subjecting the article thus produced to heat treatment to eliminate everything except a refractory residue and render the latter coherent.

3. The process which consists in forming a plastic composition consisting of fine particles held together by a cadmium alloy comprising a metal which vaporizes at a temperature substantially different from the vaporizing temperature of cadmium, squirting the same into wire, and subjecting said wire to heat treatment to eliminate the metals above mentioned and produce a coherent refractory filament.

4. The process which consists in rubbing powdered tungsten into a plastic cadmium alloy containing mercury, shaping the product into wire, and treating such wire to eliminate all components except tungsten and produce a coherent refractory tungsten conductor.

5. The process which consists in mixing refractory powder with a cadmium alloy containing bismuth, shaping the product so formed into wire, and heating said wire to eliminate the components of the alloy and produce a coherent refractory conductor.

6. The process which consists in mixing finely divided material with a cadmium-bismuth amalgam, shaping wire therefrom, and heating to eliminate said amalgam and convert the wire into a coherent refractory filament.

7. The process for the manufacture of refractory articles from finely divided material which consist in producing a coherent article of the desired shape comprising the fine particles of this material and other material intimately incorporated together, and subjecting said article to heat treatment to progressively eliminate different components of said other material concluding with a final metallic residue of relatively high vaporizing temperature and convert the article into a coherent refractory one.

8. The method for agglomerating a refractory powder into a coherent body which consists in heating a mixture of said powder with metals which vaporize at substantially different temperatures to vaporize and expel said metals successively and consolidate the residue.

9. The process which consists in subjecting a coherent body consisting of fine particles held together by coherent metallic material and containing a plurality of

metals to heat treatment to expel said metals successively and consolidate a refractory residue.

10. The process which consists in subjecting a conductor consisting of fine particles held together by an alloy comprising metals adapted to be expelled by heat at substantially different temperatures to heat treatment involving passage of current therethrough to eliminate all components of the conductor except a refractory residue and convert it into a coherent refractory body.

11. The process which consists in impregnating an amalgam which is plastic when warm with powdered refractory metal, and shaping the product so formed into ductile wire.

12. In the manufacture of incandescent filaments from powdered material by the aid of metallic material comprising a cadmium alloy, the method of producing a composition capable of being easily shaped into wires which consists in rubbing the alloy and the powder together while the alloy is warm and plastic to cause the alloy to become impregnated with the powdered material.

13. A composition for the manufacture of articles of refractory material consisting of fine particles held together by easily workable metallic material, said composition comprising metals adapted to be expelled therefrom by heat at substantially different temperatures lower than the melting point of said refractory material.

14. A composition for the manufacture of articles of refractory metal, consisting of refractory metal and other metals adapted to be expelled by heat at substantially different temperatures forming an easily workable coherent material.

15. A coherent, workable composition for the manufacture of refractory articles consisting of a cadmium alloy which is plastic when warm impregnated with powdered material.

16. The composition consisting of a cadmium alloy containing mercury and finely divided refractory material intimately incorporated together.

17. A composition for the manufacture of refractory conductors comprising a cadmium-bismuth amalgam and finely divided tungsten intimately incorporated together.

18. A conductive wire consisting of refractory metal and other metals of substantially different vaporizing temperatures forming a workable metallic material, said wire being adapted for conversion into one of coherent refractory metal by heat treatment.

19. A shaped article composed essentially of powdered material mixed with and held in place by a cadmium alloy, adapted for conversion into a coherent refractory one by heat treatment.

20. A wire comprising powdered material mixed with and held in place by a cadmium alloy, said wire containing metal that vaporizes at a temperature substantially higher than that at which cadmium vaporizes but below that at which said powdered material melts.

21. A pliant wire composed of a cadmium alloy containing mercury impregnated with finely divided material.

In witness whereof, I have hereunto set my hand this 6th day of June, 1907.

WILLIAM D. COOLIDGE.

Witnesses:
BENJAMIN B. HULL,
MARGARET E. WOOLLEY.