Oct. 15, 1929. M. N. RICH 1,731,269

PLIABLE TUNGSTEN AND METHOD OF PRODUCING THE SAME

Filed Jan. 23, 1925

FIG. 1

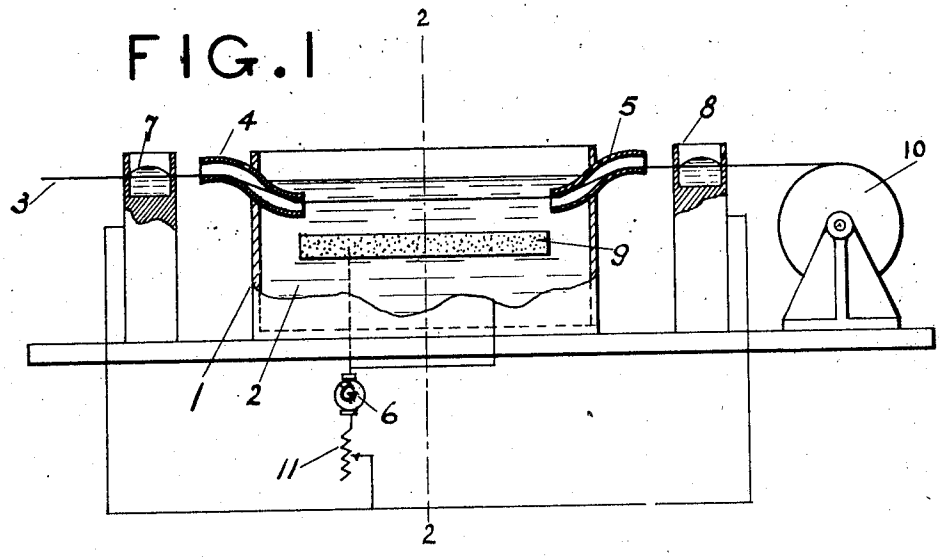
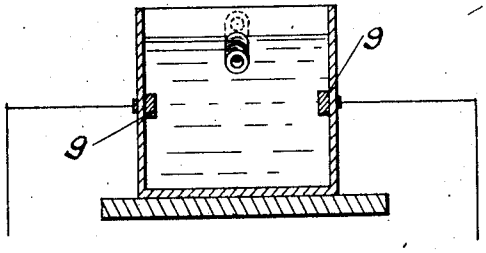


FIG. 2



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PLIABLE TUNGSTEN AND METHOD OF PRODUCING THE SAME

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This invention relates to refractory metal bodies and more particularly to tungsten bodies in a tough and pliable condition and to the method of rendering brittle tungsten bodies pliable. The invention further relates to the cleansing of the surface of tungsten or other metallic bodies from scale which has accumulated thereon during the mechanical working.

Tungsten is an extremely refractory metal and is admirably adapted for various purposes such as the production of wires for use as electric heating coils, leading-in conductors or filaments for incandescent lamps and discharge devices, and in the form of sheets or foil for the production of crucibles, plates for discharge devices, and for numerous other purposes requiring a metal capable of withstanding high temperatures.

Tungsten, however, when formed into wires, particularly wires above the 36 mil size and when made into sheets, is extremely brittle and at ordinary temperatures, can not be bent or distorted into desired shapes.

Heretofore, in order to produce various articles from tungsten rods or plates, it has been necessary to heat the metal to a high temperature. This is objectionable, however, in that the tungsten is difficult to manipulate at the temperatures required and is readily oxidized, rendering it unfit for many purposes, particularly for use in vacuum devices.

One of the objects of this invention is to produce tungsten in the form of rods or sheets pliable at ordinary temperatures.

Another object is to provide a method of rendering normally brittle tungsten rods or sheets pliable at ordinary temperatures.

A further object is to produce tungsten metal substantially free from absorbed gases and surface impurities.

Another object is to provide a method of removing gases from tungsten bodies and cleansing the surface thereof from impurities.

Other objects and advantages will hereinafter appear.

The term "pliable" is used throughout the specification and claims to define that property of the metal which renders it capable of being bent or distorted at ordinary temperatures and by which it readily adapts itself to changes of shape.

The present invention is particularly adaptable for use in connection with the method of producing ductile tungsten set forth in U. S. Patent 1,082,933, W. D. Coolidge. Briefly, the Coolidge process as applied to the production of tungsten wire consists in reducing an oxide of the metal such as tungstic oxide in hydrogen, pressing the powdered metal thus produced into slugs at extremely high pressures, sintering the slugs in hydrogen into coherent bars and swaging and mechanically working the sintered bars in hydrogen to a diameter of about 36 mils and thereafter drawing the wire into desired sizes.

The wires at the conclusion of the swaging operation are sufficiently ductile to permit them to be drawn at an elevated temperature. However, they are brittle and can be handled only with difficulty since they are easily broken at this stage of the operation. When an attempt is made to bend the swaged rods at ordinary temperatures, they shatter and before they can be distorted they must be brought to a red heat which, as stated above, is objectionable for many purposes.

Wires above the 36 mil size are particularly useful in making heating coils, electrode supports, etc., but heretofore, have not been used to any appreciable extent, due to the difficulty of forming them into the desired shape.

I have found, however, that when the swaged or drawn tungsten rods or wires are treated in accordance with the process set out in detail hereinafter, that the brittleness and tendency to shatter is eliminated and the tungsten rod or wire is rendered tough and pliable at room temperatures so that it may be readily coiled or bent into any desired form without breaking.

The rods or wire during the swaging operation, become coated with scale composed principally of carbon, oxides, etc., compacted onto the rod in a dense adherent form by the hammering of the swaging dies. Heretofore this scale has not been removed prior to the drawing operation and during such operation imposed considerable resistance to the flow of the metal under the action of the dies. How-

ever, in carrying out my invention in its preferred form, this surface scale may be entirely eliminated preceding the drawing and a more uniform and more rugged wire or filament produced as will more fully appear hereinafter.

In accordance with the present invention, brittle tungsten bodies are subjected to the action of nascent oxygen for a definite period of time and by the action of the nascent oxygen thereon are rendered pliable. While I do not desire to limit myself to any particular theory as to the action of the nascent oxygen in effecting the pliability of the metal, it appears highly probable that it is due mainly, to the elimination of hydrogen and possibly other gases or impurities from the metal. For instance, it is well recognized that absorbed hydrogen renders tungsten very brittle and I have found that when tungsten wire in a pliable condition is heated in the presence of hydrogen and thereby rendered brittle, that its pliability may be entirely regained by subjecting it to the action of nascent oxygen. I have further found that tungsten which has become embrittled by over working, that is, tungsten rendered brittle by a change in its crystalline structure, cannot be rendered pliable to any appreciable extent by nascent oxygen alone. After recrystallization or annealing of this metal, however, it may be rendered pliable by my process.

In the preferred embodiment of my invention and as a convenient method of producing nascent oxygen and subjecting the tungsten to the action thereof, I make the tungsten article the anode of an electrolytic cell utilizing as an electrolyte, a solution which evolves nascent oxygen at the anode either as a primary reaction product or as a secondary reaction product. The electrolyte should preferably be of such nature that it will hold tungsten in solution since, obviously, if tungstic acid were deposited out of the solution, it would be disadvantageous. Among electrolytes which might be mentioned as suitable for carrying out this invention, are sodium hydroxide, potassium hydroxide, sodium tungstate, etc., the first of these being preferred due mainly to its cheapness.

Whichever of these electrolytes is used, care should be taken to prevent the hydrogen evolved at the cathode from dispersing to the anode, since should the hydrogen be permitted to mingle with the nascent oxygen at the anode, it would neutralize the effect thereof and prevent or greatly hinder the removal of hydrogen from the tungsten anode. Any desired means may be provided for preventing the hydrogen from dispersing to the anode such as the use of porous compartments, baffles, separate chambers for the anode and cathode or by spacing the electrodes a sufficient distance apart to preclude any neutralizing effect of the hydrogen on the oxygen at the anode.

It is necessary to use direct current in effecting the pliability of the metal since if alternating current is used the tungsten alternately becomes an anode and cathode and the hydrogen evolved on the metal when it is a cathode prevents the oxygen evolved during the other half of the cycle from effecting the desired result.

I have also found that a fairly definite time interval is required for the oxygen to accomplish the removal of the hydrogen or other impurities to render the tungsten pliable. This time element depends on several factors, namely, the size and shape of the tungsten body, the current density thereof while serving as the anode and the extent to which the hydrogen is isolated therefrom.

The current density of the anode and the time of exposure thereof within the solution should be so regulated as to effect the pliability with a minimum solution of tungsten from the anode. The current density which I have found to produce good results with various sizes of tungsten rods or wire is about 15 amperes per square inch but this may be varied considerably and equally good results obtained. The lower the current density, the greater the time of exposure required to effect the desired result. Furthermore, with long exposure the current density must be relatively low to prevent excessive corrosion of the anode surface. I have found, however, that the time of exposure cannot be reduced below a certain definite interval regardless of the extent to which the current density is increased and therefore, in order to prevent too large a quantity of the tungsten from going into the solution from the anode, it is necessary to use the smallest current density which will effect the pliability of the metal in the desired period.

The cathode of the electrolytic bath may be composed of carbon, copper or other suitable material but preferably should be of a material which is insoluble in the solution used.

Simultaneously with the rendering of the tungsten pliable, it is cleansed of its surface carbon, oxides and impurities and rendered bright and metallic in appearance. This scale is thrown into the solution by the dissolving away of the tungsten from the surface of the anode.

The tungsten if in the form of a rod or wire may be continuously passed through the electrolyte at such a rate that its total time in the solution is just sufficient to completely remove the surface scale therefrom and render the tungsten pliable. The time of exposure may be readily determined with very little experience by observing the condition of the metal as it passes through the solution. As the tungsten enters the solution, an ebullition of

gases ensues which gradually decreases in volume as the wire progresses through the solution so that by the time it emerges therefrom, no visible reaction is taking place and the metal is bright and shiny and free of adherent gas bubbles. I prefer to maintain this point of cessation of gas ebullition a sufficient distance from the end of the bath to insure that the reaction is complete.

I am aware that heretofore, it has been proposed to ductilize tungsten which has become embrittled by over working by removing the skin or surface portion, by means of an electrolyte, such as potassium hydroxide, as set forth in U. S. Patent 1,077,696 of C. T. Fuller. While the removal of the surface of the tungsten rod or wire may to some extent permit the rod to be further drawn or swaged, it does not render over worked metal ductile nor pliable. It therefore differs essentially from my invention which is directed primarily to rendering tungsten pliable which may already be sufficiently ductile to be further swaged or drawn but because of extreme brittleness cannot be bent or distorted.

In order that this invention may be more fully understood, reference is had to the accompanying drawing in which;

Fig. 1 is a side elevational view of apparatus for continuously ductilizing tungsten wire; and,

Fig. 2 is a section on the line II—II of Fig. 1.

The apparatus shown in Fig. 1 for carrying out the process, comprises a receptacle 1 containing an electrolyte 2 such as sodium hydroxide or potossium hydroxide or other material capable of evolving oxygen at the anode and preferably one that has a solubility for tungsten salts. The wire 3 is introduced into the electrolyte 2 through a tube 4 and passes from the electrolyte through a corresponding tube 5 although other suitable means for passing the wire through the solution may be provided. The wire 3 constitutes the anode of the bath and is connected electrically to a suitable source of current, such as a generator 6, by means of a pair of mercury contacts 7 and 8 arranged at each end of the receptacle 1. The cathode 9 which may be in the form of a pair of plates of carbon or copper or any other suitable material which will not react chemically with the electrolyte are arranged on opposite sides of the wire 1 at a sufficient distance therefrom so that hydrogen, evolved by the cathode, will not disperse to the anode. I have found that a distance of four inches is sufficient for this purpose. The wire 3 as it is drawn through the bath may be coiled upon a reel 10 or other suitable winding device.

The voltage applied to the wire 3 as it passes through the bath may be controlled by a suitable rheostat 11 or other voltage regulating means and it should be of such value that the current density of the rod or wire 3 will be sufficiently high to cause the evolution of a considerable quantity of oxygen thereon. It should not be excessive, however, since too great a quantity of tungsten will be caused to go into the solution from the rod or wire.

The current density which I have found to produce good results with wires of various sizes is approximately 15 amperes per square inch although it is to be understood that the current can be varied within wide limits and excellent results obtained. For 3 mil tungsten wire using the current density given above, the time of exposure required to treat the wire, is about 90 seconds, while with 6 mil wire only about 20 seconds is required. The process is not limited to small wire, however, since brittle wire as large as 70 mil has been rendered tough and pliable by my process.

An application of this process may be found in the production of tungsten filaments for incandescent electric lamps. Difficulty has been experienced heretofore in the production of such filaments due to the irregularities in the cross section thereof, causing what are known in the art as hot spots or spots of high resistance. When the filament is incandesced, these spots of high resistance are unduly heated and cause the filament to prematurely burn out. These hot spots are believed to be largely due to irregularities produced in the swaged rod by the swaging dies and which have not been entirely eliminated during the drawing process. The swaged rods are not smooth but are covered with innumerable depressions which are filled with impurities driven therein by the swaging dies. These impurities impose a resistance to the flow of the metal through the drawing dies so that the marks made by the swaging dies are not eliminated in the drawing process. I have found that by removing this surface scale and dirt from the swaged wire and rendering the wire pliable in accordance with the process described herein, that the filaments produced therefrom are more uniform in cross section and hot spots are substantially eliminated, thus resulting in a more rugged filament, having a longer life.

Sheets of tungsten or tungsten foil rendered pliable in accordance with this invention may be bent at ordinary room temperatures, into various shapes for use as plates for radio tubes, etc., or may be pressed or spun into convenient shapes for use for various purposes such as crucibles.

Obviously, many other applications of this process will be apparent and while the invention has been described particularly with reference to the rendering pliable and cleansing of tungsten wires or sheets, it is not so limited but may be applied to a variety of objects composed of tungsten metal or of

other metals and obviously, many changes may be made in the process as set forth herein without departing from the invention.

What is claimed is:

1. The method of rendering tungsten pliable which has become embrittled by the absorption of hydrogen consisting in utilizing the tungsten as the anode of an electrolyte which on passage of current therethrough, evolves nascent oxygen at the anode and hydrogen at the cathode and preventing the dispersion of the hydrogen from the cathode to the anode.

2. The method of rendering tungsten pliable which has become embrittled by the absorption of hydrogen consisting in utilizing the tungsten as the anode of an electrolyte which on passage of current therethrough, evolves nascent oxygen at the anode and hydrogen at the cathode and spacing the anode and cathode a sufficient distance apart to prevent dispersion of the hydrogen to the anode.

3. The method of rendering tungsten pliable which has become embrittled by the absorption of hydrogen consisting in utilizing the tungsten as the anode of an electrolyte composed of an alkaline solution and preventing dispersion of hydrogen to the anode from the cathode.

4. The method of rendering tungsten pliable which has become embrittled by hydrogen which consists in utilizing the tungsten as the anode of an electrolyte composed of sodium hydroxide and preventing dispersion of hydrogen to the anode from the cathode.

5. The method of rendering pliable, metals embrittled by the absorption of hydrogen consisting in utilizing the metal as the anode of an electrolytic bath and preventing dispersion of hydrogen to the anode.

In testimony whereof, I have hereunto subscribed my name this 22nd day of January, 1925.

MALCOLM N. RICH.