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HARDENING REFRACTORY METALS

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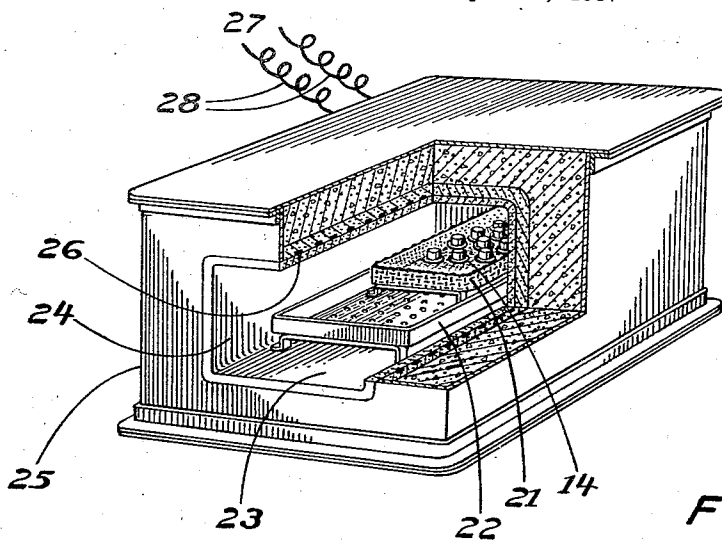


FIG. 1

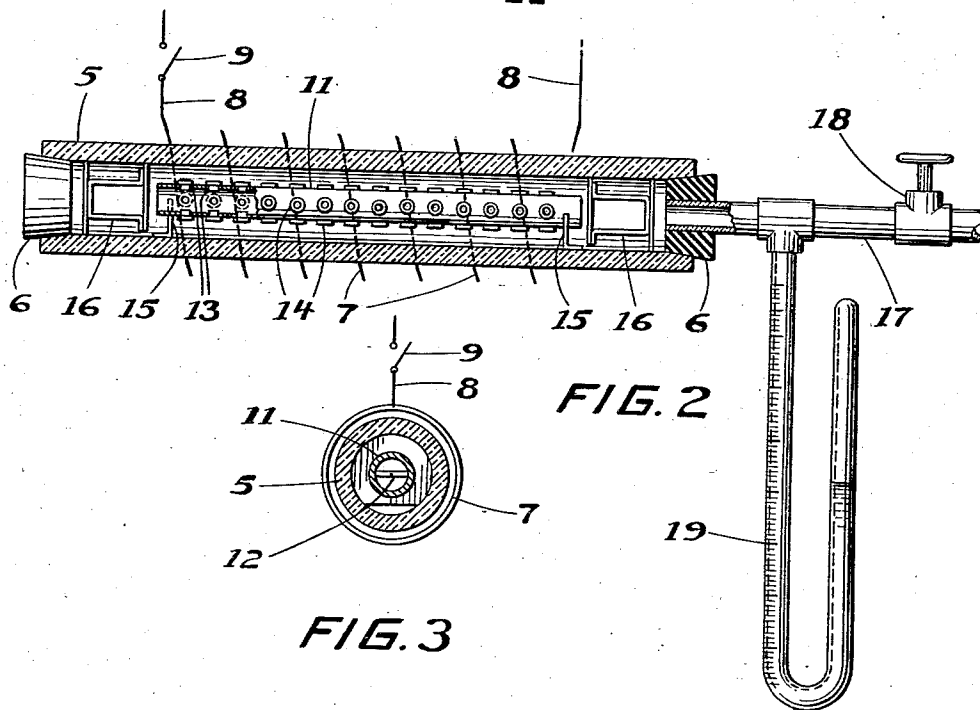


FIG. 2

FIG. 3

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HARDENING REFRACTORY METALS

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7 Claims. (Cl. 148—13.1)

This invention relates in general to hardened refractory metals and has more particular reference to hardened tantalum and a method of hardening same.

5 A primary object of the present invention is the provision and production of hardened tantalum and useful articles thereof.

An important object of the present invention is the provision of a uniform method of more
10 precisely controlling the hardening of tantalum and tantalum articles.

An additional object of my invention is the provision of a method for hardening tantalum articles which will preserve the exact original
15 shape and polish after the completion of the hardening operation: that is to say, that by my new method I am able to harden a tantalum article while maintaining the dimensions and surface polish substantially as originally produced.
20 This is extremely important where the article is small and finished to exact dimensions.

A further important object of the invention is the provision of tantalum articles having a hardened skin and a soft interior, and further
25 the production of tantalum articles having a graduated hardness varying from the outside in, and a novel method of producing tantalum or tantalum articles having the desired hardness.

Other objects and advantages of the invention
30 will be apparent from the following description and from the accompanying drawing, in which similar characteristics of reference indicate similar parts throughout the several views.

In the drawing:

35 Fig. 1 is a partly diagrammatic view, in perspective, of one type of apparatus suitable for treating the refractory metal and articles thereof in accordance with the invention.

40 Fig. 2 is a diagrammatic view of other apparatus suitable for treating the said refractory metal; and

45 Fig. 3 is a transverse sectional view of a heating element suitable for use in my novel method and showing a refractory metal in place for the hardening operation.

50 There are various uses to which a substantially non-corrosive and wear-resisting hard metal may advantageously be put, for example: spinnerets used in the manufacture of artificial silk or rayon, which are provided with fine circular openings or apertures. These spinnerets are subjected in use to acid solutions and must therefore be non-corrosive or acid-resisting, hard and durable, or wear-resisting, because if the openings are even
55 slightly distorted or flat the rayon produced will

be of inferior and improper quality and will consequently cause a pecuniary loss when sold.

Other uses of hard, non-corrosive and durable metals will be apparent, the foregoing embodiment being recited merely by way of example, for
5 instance: bushings, extrusion jaws, hypodermic needles, needle valves and valve seats; electrical instrument pivots, pen points, thread guides, spindles, swivel pins, turbine blades, nozzles, injectors, orifice plates, and many other articles
10 for use in the chemical and electrical industries where the articles in use are subject to wear and/or corrosion.

The desirable properties of tantalum have already caused this material to be much favored for
15 such uses, but in many instances it is desirable to have a material with the non-corrosive or acid-resisting and hard qualities of tantalum together with a greater degree of hardness, durability or wear-resisting qualities and workability.
20

It has been suggested to provide a material harder than tantalum and with some of its properties by alloying tantalum with a harder material, such as tungsten, or by alternately heating
25 and hammering tantalum. The tantalum-tungsten alloy is not wholly satisfactory for such uses, because the degree of hardness is not readily controllable and the resulting properties of such an alloy are not altogether desirable. Moreover,
30 such an alloy is relatively expensive to produce, and does not possess the degree of hardness required for such uses, and it is not readily workable. As a matter of fact, such alloy can be further increased in hardness by my new process.

It is not economically feasible to harden tantalum by alternately heating and hardening, nor
35 is it possible to harden uniformly an irregular body by such treatment. Furthermore, such method must be carried out so painstakingly that it is highly impractical and subject to such limitations as to make it substantially unworkable.
40

Four methods of hardening tantalum have been suggested in the prior art, namely, heating the tantalum in air at atmospheric pressure, heating tantalum in an atmosphere of a gas
45 which tends to combine with the tantalum to produce a hard composition, heating and quenching the tantalum, and heating the tantalum in substantially a vacuum to a temperature in excess of that required for air hardening, and there-
50 after admitting to the vacuum limited quantities of air or other hardening gas.

The first three of these methods have been thoroughly investigated, and it has been found that no useful hardness of tantalum could be obtained

but that a vigorous reaction occurred at the surface of the tantalum with very little penetration of the gases to the interior of the tantalum. Moreover, such methods discolor the tantalum and frequently produce rotten or brittle metal. The fourth method, disclosed in the Austin patent, 2,015,509, although entirely successful for some purposes, is not subject to as precise control as is desirable and is not capable of producing as uniform results as the present process.

Briefly, the invention contemplates a novel method for overcoming the foregoing objections and producing tantalum or articles made therefrom having a varying degree of hardness from the outer surface inwardly, a degree of hardness more uniformly distributed throughout the section of the tantalum or tantalum article than heretofore realized, or a hardened case on the tantalum or article made therefrom.

In order to accomplish the foregoing objects, I heat tantalum or tantalum objects, which have preferably been previously annealed, by heating in an atmosphere of less than atmospheric pressure, to a low temperature in an atmosphere of hardening gas, for example, air, for an extended period of time. This tantalum is then weighed to determine whether sufficient gas has been taken up, and if necessary the heating operation is repeated until the necessary gain in weight has been made. Thereafter I transfer the tantalum to a vacuum heating chamber and raise the temperature of the tantalum above the initial heating temperature and maintain the same until the absorbed air or other gas has been diffused and distributed through the body as much as is desired. The degree of hardness is apparently determined by the amount or quantity of gas absorbed by the tantalum, and is further influenced by the time of soaking under reduced pressure. The degree of hardness and the relative hardness throughout the tantalum body may therefore be controlled by the time and temperature of initial heating in the gaseous atmosphere and by the control of the time and temperature during the soaking period.

It will, of course, be apparent that a hardened case may be formed on the tantalum or tantalum articles by control of the initial heating, and by restricting the soaking period thereafter, and this hardness may be made to vary from the surface of the tantalum body inwardly thereof by controlled soaking periods until such time as the gas is uniformly distributed throughout the section of the article, at which time the material is uniformly hardened.

While I do not wish to limit my invention to any particular apparatus for accomplishing the novel results, I have illustrated by way of example in the drawing, suitable devices for hardening tantalum.

The tantalum articles to be hardened, for example, spinneret cups 14, are distributed more or less evenly in trays 21 and 22 which are so arranged on the floor 23 of the muffle 24 that unrestricted access to the air is obtained. The muffle furnace 25 is of generally conventional construction consisting of a ceramic muffle 24 wound with any suitable resistance wire 26 and heated by electric current from source 27 through suitable leads 28. The construction of the furnace 25 forms no part of my invention and its construction is merely indicated in order to demonstrate the carrying out of the invention. The tantalum articles may, for example, be placed in a cold furnace, and in such case the current

may be supplied to the furnace at as high a rate as will permit even heating until the temperature has reached the order of 450° C. Thereafter the current is applied more cautiously until the temperature of the order of 480 to 500° C. has been reached. Heating at this peak temperature is continued from two to five or more hours, depending upon the desired degree of hardness and the maximum cross section of the article heated. If the temperature exceeds 600° C. or if the heating is prolonged unnecessarily, the articles will react with too large a quantity of air, thereby fatally embrittling the same.

It is obvious that if it is desired to harden the tantalum with another gas than air the atmosphere of the muffle furnace 25 may be suitably controlled by closing the same to air, and passing the desired gas through the muffle.

When the articles have attained the desired increase in weight, they are withdrawn from the muffle furnace and transferred to the soaking furnace. Said soaking furnace may be suitably of the type employed by Austin, as disclosed in his Patent 2,015,509. This apparatus comprises any suitable heating unit or furnace capable of developing the desired temperatures and of providing a heated vacuum chamber, such, for example, as a quartz tube 5 closed at each end by means of rubber stoppers or caps 6 and provided with a source of heat which I have illustrated as an external coil 7 encircling the quartz tube and connected by means of conductors 8 to a suitable source of electric potential, not shown. The electric energy supplied to coil 7 may be controlled by any suitable switch 9, as shown in the drawing. A frame, receptacle or holder 11 of any suitable metal capable of withstanding the temperature developed within the quartz tube 5 is provided for carrying the tantalum or tantalum articles to be treated. This holder or receptacle 11 is preferably of tantalum or any other suitable high melting point metal or alloy, and is illustrated as a cylinder carrying tantalum strips or articles 12 as shown in Figure 3, or the tantalum cylinder may be provided with a plurality of apertures 13 as shown in Figure 2 for carrying the plurality of spinnerets or other tantalum articles 14.

This holder or receptacle carrying the tantalum or articles to be hardened is inserted in the tube 5 and may be supported therein by any suitable means such as brackets 15 at each end of the tantalum receptacle. Where the stoppers or caps 6 are constructed of an inflammable material they may be protected from the heat within the quartz tube 5 by means of heat baffles or reflectors 16, positioned at each end of the quartz tube between the stoppers or caps 6 and the corresponding ends of the receptacle or holder 11.

The interior of the quartz tube 5 is connected by means of a tube 17 or any other suitable connector passing through one of the stoppers 6 to any suitable vacuum pump, not shown, for the purpose of reducing or exhausting the atmosphere within the tube 5. The action of the vacuum pump on the interior of the tube 5 is controlled by a valve 18, which at the beginning of the operation is open, and the pump is operated to reduce the pressure within the tube 5 to about 1 millimeter of mercury, which reduced pressure is maintained until the tantalum or tantalum articles are heated to from 1000° to 1400° C. by means of the heating coil 7. This pressure may be indicated by any suitable pressure-indicating mechanism, such as a manometer 19 connected 75

to the tube 17, as shown in Fig. 2, and the heating of the tantalum or tantalum articles is continued for 15 minutes to a half hour. The switch 9 is then opened and the valve 18 may be closed and the pump shut down. The apparatus is then permitted to regain its normal temperature either by itself, or cooling may be hastened by any desirable means. When the temperature has been sufficiently reduced, say below 300° C. the apparatus may be safely opened and the hardened articles removed therefrom.

The time and temperature of heating in the throughout the metal, the same degree of hardness may be determined by experiment, and I have found that for the commercially desirable hardness range an increase of weight of from .05% to .15% is normally satisfactory. If the soaking is continued until the air is diffused air required to produce the desired degree of springiness mentioned by Austin in his patent, above referred to, is obtained. On the other hand, if the soaking is carried on for a limited time, a hard surface is produced while the core remains soft. The remainder of the body possesses a graded hardness from the outside in.

As pointed out, moderate hardening of either the surface or the whole body may be obtained by reducing the air treatment, and greater hardening is obtained by more prolonged heating. Metal or articles when soaked even for only a limited time take on a bright metallic appearance, and the dark oxide coat gradually disappears as the gas penetrates into the metal. If the gassing is only moderate the metal can still be worked by rolling or swaging to produce additional work-hardness or to alter the shape.

While I have described the novel method as applied to tantalum, it is understood that other similar metals and alloys such, for example, as columbium, and tantalum and/or columbium alloys, in which the tantalum and/or columbium predominates, may be treated in the same manner, and other gases known to harden tantalum, such as nitrogen or oxygen may be substituted for air; and that I am not limited to the details as hereinabove set forth except as defined by the following claims.

I claim:

1. A method of gas hardening a hard refractory metal from the group consisting of tantalum, columbium and alloys predominating in one or both of tantalum and columbium which comprises degasifying said metal by heating it at a reduced pressure to from 1000 to 1400° C. supplying an atmosphere of hardening gas of the class consisting of air, nitrogen and oxygen at a temperature not exceeding 500° C. until the desired amount of gas has been taken up, and continuing the heating at a more elevated temperature under a reduced pressure of not more than a few millimeters of mercury until the absorbed gas has been substantially diffused into the metal body.

2. A method of hardening a hard refractory metal from the group consisting of tantalum, columbium and alloys predominating in one or both of tantalum and columbium which comprises supplying an atmosphere of air at a temperature not exceeding 500° C. until the desired amount of gas has been taken up, and continuing the heating at a more elevated temperature under reduced pressure of not more than a few millimeters of mercury until the absorbed gas has been substantially diffused into the metal body.

3. A method of hardening a hard refractory metal from the group consisting of tantalum,

columbium and alloys predominating in one or both of said metals by diffusing a regulated amount of gas through the metal which comprises heating the hard refractory metal to the degasified temperature thereof while maintaining such an atmospheric pressure as will remove the occluded gases from the hard refractory metal; reducing the temperature of the hard refractory metal while maintaining the sub-atmospheric pressure until the temperature has fallen so low that air will not react with the hard refractory metal; heating the hard refractory metal in an atmosphere of hardening gas to a temperature of the order of 500° C. and less than 600° C. until the hard refractory metal has absorbed such an amount of gas as will provide the desired hardness upon diffusion; heating the so treated hard refractory metal under reduced pressure to a higher, gas diffusing temperature until substantially uniform diffusion is obtained, and maintaining the reduced pressure until the hardened hard refractory metal has cooled below the reaction temperature of air with said hard refractory metal.

4. A method of hardening a hard refractory metal from the group consisting of tantalum, columbium and alloys predominating in one or both of said metals by diffusing a regulated amount of air through the metal which comprises heating the hard refractory metal in the air to a temperature of the order of 500° C. and less than 600° C. until the hard refractory metal has absorbed such an amount of air as will provide the desired hardness upon diffusion; heating the so treated hard refractory metal under reduced pressure to higher, gas diffusing temperature until substantially uniform diffusion is obtained, and maintaining the reduced pressure until the hardened hard refractory metal has cooled below the reaction temperature of air with the hardened refractory metal.

5. A method of gas hardening a hard refractory metal from the group consisting of tantalum, columbium and alloys predominating in one or both of tantalum and columbium which comprises heating the metal at a temperature not exceeding 500° C. while supplying an atmosphere of a hardening gas of the class consisting of air, nitrogen and oxygen until the desired amount of gas has been taken up and continuing the heating at a more elevated temperature under a reduced pressure of not more than a few millimeters of mercury until the absorbed gas has been substantially diffused into the metal body.

6. A method of hardening a hard refractory metal from the group consisting of tantalum, columbium and alloys predominating in one or both of said metals by diffusing a regulated amount of nitrogen through the metal which comprises heating the hard refractory metal in an atmosphere of nitrogen to a temperature of the order of 500° C. and less than 600° C. until the hard refractory metal has absorbed such an amount of gas as will provide the desired hardness upon diffusion, and heating the so treated hard refractory metal under reduced pressure to a higher gas diffusing temperature until substantially uniform diffusion is obtained.

7. A method of hardening tantalum which comprises heating said tantalum in air for one to five hours at from 450° to 500° C. and then heating the air treated tantalum in a vacuum up to one-half hour at above 1000° C.

CERTIFICATE OF CORRECTION.

Patent No. 2,170,844.

August 29, 1939.

LILLIAN M. VAN NOTE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 13, strike out the words "throughout the metal, the same degree of" and insert the same after "diffused", line 18; line 19, strike out "air required to produce the desired degree of" and insert the same after "the" second occurrence, line 12; and second column, line 36, claim 4, before "higher" insert a; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of October, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.