Nov. 29, 1949 W. C. LILLIENDAHL 2,489,912

METHOD OF PRODUCING TUNGSTEN ALLOYS

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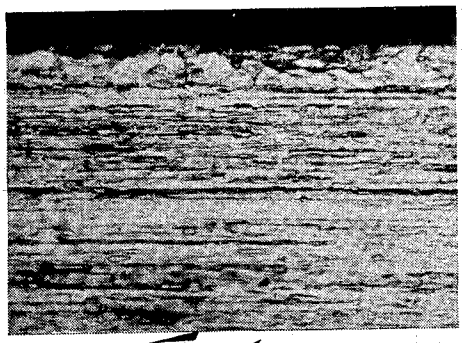


Fig. 1.

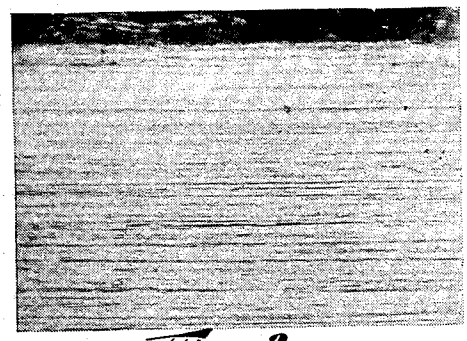


Fig. 3.



Fig. 2.

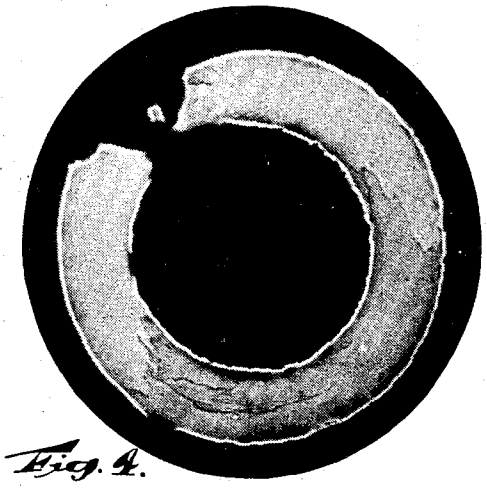


Fig. 4.

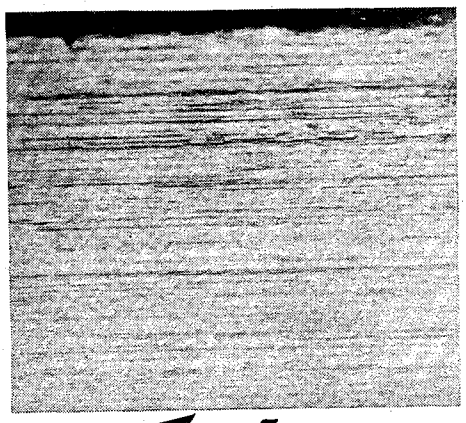


Fig. 5.

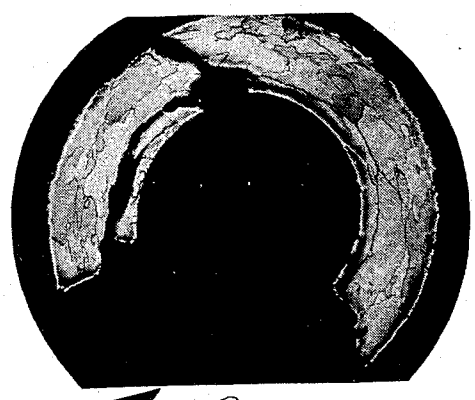


Fig. 6.

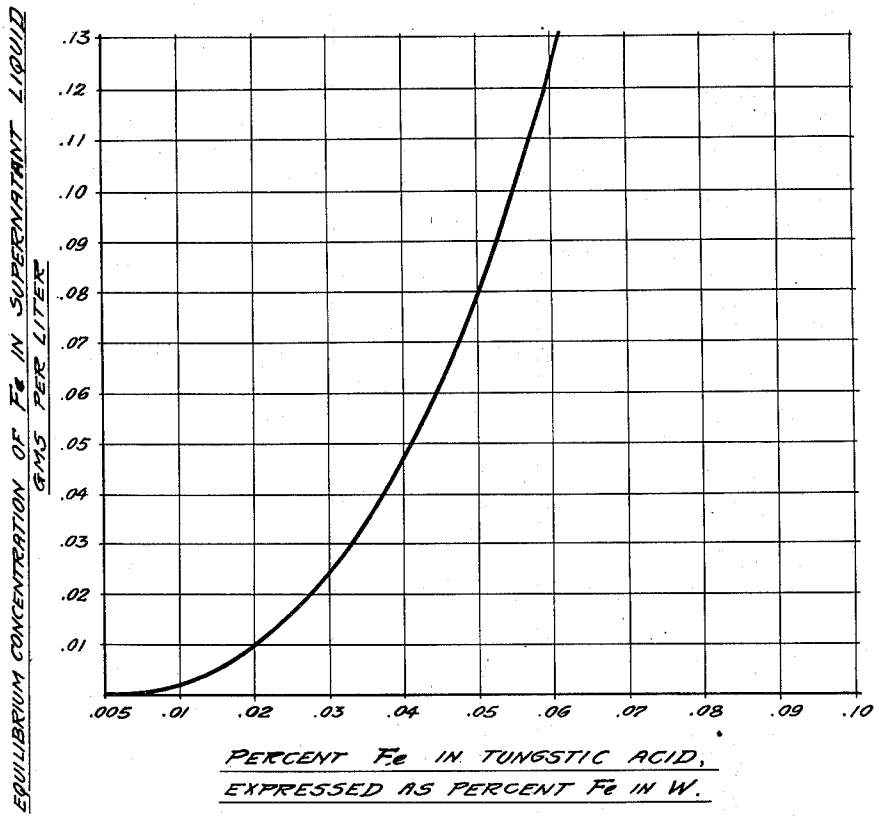
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METHOD OF PRODUCING TUNGSTEN ALLOYS

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Fig. 2.



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METHOD OF PRODUCING TUNGSTEN ALLOYS

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Application December 13, 1941, Serial No. 422,810

10 Claims. (Cl. 75—22)

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This invention relates to producing tungsten alloys and more particularly to producing tungsten alloys suitable for use in making metal filaments for incandescent filament lamps.

One of the objects of the present invention is to produce a tungsten filament having substantially the relatively high operating temperature characteristic of pure tungsten containing small amounts of silica and potassium chloride grain-benefiting constituents, which is further characterized by having a recrystallization temperature in the severely cold-worked condition substantially above the normal annealing temperature employed in the art in heat treating the cold-worked tungsten to eliminate therefrom the cold working strains, which temperature normally lies within the range 1500–1600° C.

Another object of the invention is to produce a tungsten alloy which is characterized by having a recrystallization temperature in the severely cold-worked condition materially above that of substantially pure tungsten.

Still another object of this invention is to produce an improved filament for incandescent filament lamps, the said filament being formed of a tungsten alloy containing small amounts of silica and potassium chloride grain-benefiting constituents, together with iron within the range .020 to .035%, the said filament being characterized by having a recrystallization temperature materially above the normal annealing temperature of substantially pure tungsten.

Other objects and advantages will be apparent as the invention is hereinafter more fully disclosed.

In accordance with these objects I have discovered that the addition of iron to substantially pure tungsten containing small amounts of silica and potassium chloride grain-benefiting constituents, each in the relative amounts heretofore employed in the production of substantially pure tungsten characterized by an interlocking crystal structure known in the art as nonsag wire, in an amount in excess of about .020% but not in excess of the solubility limit of the iron in tungsten at the normal operating temperature in an incandescent filament lamp, has a marked and unexpected effect upon the recrystallization characteristics of the wire.

This effect can most simply be described as being an increase in the recrystallization temperature of the tungsten, without substantial decrease in the melting point, as compared with that of pure tungsten. This beneficial effect is most marked in tungsten in the severely strain-

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hardened condition. As a result of this beneficial effect of the iron, the severly strain-hardened tungsten may be subjected to heat treatment at temperatures as high as about 1600° C. for time intervals adapted to eliminate therefrom the major portion of the cold working strains, without recrystallization of the cold worked grains. This characteristic imparted by iron within the range above given, greatly facilitates the mechanical deformation of the tungsten to filamentary form and produces a final filament of more uniform and consistent physical and recrystallization characteristics than heretofore obtainable in the art.

The addition of iron in an amount up to about .060% to tungsten metal powder prior to sintering also has been found to improve the grain structure of tungsten in the so-called ingot or sintered form, in that iron in this amount appears to effect a grain refinement in the sintered ingot and facilitates the mechanical deformation of the ingot to the desired filamentary sizes.

The present invention, therefore, contemplates the addition of iron, in an amount up to about .060%, to tungsten metal powder, as well as the formation of a tungsten-iron alloy containing preferably between .020 to .035% iron.

The exact reason for, and the mechanism of, the improvement produced by iron additions to tungsten within the range specified is not clear. It is preferable to introduce the iron into the tungstic acid at the time grain benefiting constituents, such as silica and potassium chloride, are introduced, to obtain this desired result, and to introduce initially into the tungsten approximately three times the minimum amount of iron which is desired in the finished filament, to allow for losses encountered during reduction, sintering, high temperature mechanical deformation, and heat treatment operations common in the art.

My tests have shown that iron within the range .020 to .035% in the final substantially pure tungsten filament, substantially inhibits or suppresses recrystallization in the most severely strain-hardened drawn tungsten filament at temperatures below about 1600° C., and that in the absence of iron or with iron below about .020%, this desirable condition in the severely cold-worked tungsten is not obtained.

Moreover, my tests have indicated that iron, in amounts much higher than about .035% in the final filament, is detrimental to stability as an incandescent lamp filament, for the reason that its melting point is materially lowered and

excessive blackening of the lamp bulb occurs when the filament is operated at the usual high temperature common in the art. Iron within the range .020 to .035% does not materially lower the melting point of tungsten and moreover appears well within the solubility limit of iron in tungsten at the usual high operating temperatures at present employed. In its broadest concept the present invention aims to provide in the tungsten an amount of iron, at least about .020% which is within the solubility limit of iron in tungsten at the normal high operating temperature of about 2500° C. My experiments have so far indicated that .035% is about the maximum percentage of iron permissible to obtain this result, but it may be slightly higher.

In accordance with the present invention, by limiting the iron content to an amount not in excess of the solubility limit of iron in tungsten at the normal high operating temperature now employed in incandescent filament lamps, but at least above about .020%, none of the defects accompanying the use of iron within the range specified in the Fonda Patent #1,496,457, dated June 3, 1924, occur. Instead, this lower range of iron appears to stabilize the recrystallization characteristics of the severely cold-worked metal to such an extent as to materially facilitate all annealing operations during cold mechanical deformation, thereby insuring the ultimate production of a severely strain-hardened filament which is substantially uniformly strained throughout its cross-section and length, and a finally annealed filament or coil which is consistently and uniformly unrecrystallized and consistently uniformly responsive to a predetermined recrystallization heat-treatment designed to develop therein a predetermined crystal structure found preferable for extended life at the normal high operating temperatures employed during use. Heretofore in the art, this has not been obtained.

In the formation of coil type filaments from the iron and tungsten alloy of the present invention, the full benefit of the effect of the iron is obtained. The usual practice in the forming of coil type filaments is to wind the filament in its severely cold-worked condition into coils on a mandrel and then anneal the coils while they are still on the mandrel to set the coil turns and condition them for mounting in the lamp. Thereafter, following the usual exhaust and sealing-in operations, the metal coils are subjected to a sequence of heating operations designed to effect recrystallization and grain growth of the annealed severely cold-worked grains into a grain structure having a relatively high stability at the operating temperature of the lamp.

It is customary at the conclusion of the coil-winding operation to anneal the coils at a temperature within the range 1500 to 1600° C. for a time interval sufficient to obtain strain relief without recrystallization, as any recrystallization of the cold-worked metal during this heat treatment results in so-called brittle coils which cause excessive manufacturing losses during mounting and a large proportion of defective lamps during subsequent exhaust and sealing-in operations. Furthermore, coils which during this coil annealing operation have been heated to a temperature for a time sufficient to effect a partial recrystallization, even though the extent of such recrystallization is insufficient to impart brittleness to the coil, invariably show inconsistent results on subsequent life test as compared to the coils in which the annealed metal is un-recrystallized owing to the marked difference in crystal structure produced in the partially recrystallized metal as compared to un-recrystallized metal during the so-called seasoning treatment.

The determination of the maximum temperature to which the coils may be heated during annealing to obtain within any given time strain relief without recrystallization is exceedingly difficult even under the most standardized of manufacturing conditions. I have found that the iron content within the range specified inhibits, retards, or prevents recrystallization of the tungsten even in its most severely strain-hardened condition at temperatures as high as about 1600° C. and that coils formed from the tungsten-iron alloy of the present invention may be safely annealed within the temperature range 1500 to 1600° C. for time intervals sufficient to obtain strain relief and coil set without any recrystallization of the severely strain-hardened metal and that, following the mounting, exhaust and sealing-in operations, the annealed coils are uniformly responsive to recrystallization heat treatment operations to consistently develop therein a large grain interlocking crystal structure such as is desired for consistently long life at the relatively high operating temperature at present employed in incandescent filament lamps. Moreover, my experiments indicate that the particular grain structure developed on recrystallization of the annealed coils of the tungsten-iron alloy of the present invention may be varied consistently by appropriate variations in the heat treating temperatures and times in the so-called seasoning schedule employed.

As an example of the marked improvement of the present invention over the substantially pure tungsten filaments heretofore employed, reference should be made to the accompanying drawings wherein:

Figs. 1 and 2 are photomicrographs which illustrate in longitudinal section, respectively at 750 and 60 magnifications, the typical grain structure of the annealed wire and seasoned or recrystallized coil filament, consisting of substantially pure tungsten of the type known in the art as non-sag wire;

Figs. 3 and 4 illustrate in longitudinal section, respectively at 750 and 60 magnifications, the grain structure of the same kind of tungsten, as illustrated in Figs. 1 and 2, but containing .020% iron in accordance with the present invention;

Figs. 5 and 6 illustrate in longitudinal section, respectively, at 750 and 60 magnifications, the grain structures obtained in tungsten metal of the type illustrated in Figs. 1 and 2 but containing .035% iron; and

Fig. 7 is a graph illustrating another feature of the present invention.

Referring to Figs. 1 and 2, the annealed structure of Fig. 1 is characterized by a surface area of recrystallized metal and by the appearance of recrystallized metal throughout the body of the metal lying inwardly from the recrystallized surface area (at the upper edge of the section). The longitudinal section shown is at 750 magnifications and the particular filament from which this photomicrograph was taken had been heated in hydrogen for ten minutes at 1500° C. The photomicrograph of Fig. 2 shows the final crystal structure obtained in a larger size wire of the same material which was formed into a coil suitable for use in a 1000 watt stereopticon lamp. This coil was annealed in hydrogen at a temperature approximating 1100° C. for about 10 minutes, and

subsequently subjected to the following seasoning schedule commonly applied to this type of coil for the purpose of recrystallizing the metal to a structure which has been found to consistently result in a long burning life:

30 volts for 3 seconds
60 volts for 3 seconds
90 volts for 3 seconds
120 volts for 3 seconds

The crystal structure indicated in the photomicrograph of Fig. 2 is that characteristic of the type of crystal structure normally obtained from wire of this type.

Referring now to Figs. 3 and 4 the crystal structures shown in the photomicrographs are those of filament formed of the tungsten-iron alloy (Fe .020%) of the present invention on being subjected to the same treatment accorded the metal structures of Figs. 1 and 2. The cold-worked structure of the metal shown in Fig. 3 extends from the interior of the filament to the surface (at the upper edge of the section) without any indication of recrystallization as far as can be ascertained from the magnification employed (750). This particular sample was also annealed by heat treatment in hydrogen at 1500° C. for ten minutes as was the sample illustrated in the photomicrograph of Fig. 1.

Referring to Fig. 4 the coil section shown is distinctly superior to and different from the crystal structure of the coil illustrated in Fig. 2. The coil was formed from a wire of the cold-worked material illustrated in Fig. 3 of the same size (11 mil.) employed in the forming of the coil of Fig. 2 and subjected to the same annealing treatment and the same seasoning schedule given the coil of Fig. 2.

It may be noted from the photomicrograph that the treating schedule normally applied to metal of the partially recrystallized type indicated in Fig. 1, produces an entirely different type of crystal structure when applied to an annealed metal wherein the annealing operation has not resulted in any recrystallization (interiorly or along the surface) of the severely strain-hardened metal. The treating schedule when applied to un-recrystallized metal results in the formation of an abnormally large interlocked crystal structure, the interlocked area of the crystals generally being characteristic of this type of tungsten metal (non-sag wire) but the individual crystals extend substantially across the section of the wire. This structure is particularly suited for high stability over a prolonged time interval at the relatively high operating temperatures now employed in incandescent filament lamps, as the possibility of growth between the grains at the operating temperature is relatively low.

Figs. 5 and 6 show the crystal structures obtained in a substantially pure tungsten of the type known as non-sag wire, containing approximately .035% iron, when subjected to the same treatment as given to the two samples of Figs. 1–2 and 3–4, respectively. The photomicrograph of Fig. 5 clearly shows that the heat treatment of the severely cold-worked metal at a temperature of 1500° C. for ten minutes in hydrogen has not resulted in any recrystallization, as obtained in the substantially pure tungsten similarly treated and shown in Fig. 1. The crystal structure indicated in the coil section of Fig. 6, while different from the structure indicated in the coil section of Fig. 4 is substantially superior to the structure obtained under identically the same conditions from the annealed material shown in Fig. 1.

This difference in the crystal structures of the material of Figs. 4 and 6 is indicative primarily that the annealing temperature was either not high enough to substantially remove all of the working strains, or the time interval of annealing was not long enough to accomplish this result at the annealing temperature employed. The retention of residual working strains in the cold-worked structure of Fig. 5 would normally tend to interfere with the normal recrystallization characteristics of the strain-hardened metal sufficient to produce a different grain structure from that shown in Fig. 4. The higher iron content of the metal of Fig. 6 also may have an effect on the recrystallization characteristics of the wire. However, in accordance with well recognized metallurgical principles, the specific grain structure from the annealed but un-recrystallized metal of Figs. 3 and 5, is obtainable by appropriate control over the time-temperature conditions during recrystallization heat treatment.

In the manufacture of the tungsten iron alloy of the present invention, I prefer to produce the tungstic acid for reduction to tungsten metal powder by the method described and claimed in the Driggs Patent No. 1,965,222 of July 3, 1934, modified by the practice described and claimed in the Highriter et al. application Ser. No. 405,682, filed August 6, 1941, now Patent No. 2,316,583, dated April 13, 1943, as further modified by the practice hereinafter described, and to reduce the tungstic acid (or oxide obtained therefrom) to metal powder and to convert the metal powder to filament in accordance with standard methods heretofore known in the art. I have found, however, that iron within the range desired for the above beneficial result also has a beneficial result on the grain structure and working properties of the tungsten sintered ingot formed as above indicated. It has been heretofore well known and disclosed by the Fonda Patent No. 1,496,457 that iron volatilizes at the usual temperatures employed in sintering and heat treating tungsten metal powders. My experiments have indicated that in order to obtain an iron content within the range .020 to .035% in the finished filament it is necessary to incorporate about 3 times the minimum amount desired in the tungsten metal powder prior to sintering, or about .060%.

Preferably, this amount of iron is introduced into the tungstic acid following precipitation and while the acid is still wet, in accordance with the general practice described and claimed in the Driggs Patent No. 1,965,222 dated July 3, 1934, modified as hereinafter described.

I have found that the addition of a water-soluble and hydrogen-reducible iron salt to the tungstic acid slurry, together with the silica and potassium chloride grain benefiting constituents of the Driggs invention results in the introduction of a new variable, namely, selective adsorption.

I have found that the amount of iron adsorbed by the tungstic acid in accordance with the general teaching of the Driggs patent is a function of the concentration of the iron in the supernatant liquid plus an adsorption factor depending upon physical properties of the precipitated tungstic acid in the slurry. The relative amount of iron adsorption by the tungstic acid is at a maximum for low concentrations of iron in the supernatant liquid and decreases with increasing

concentration of iron in the supernatant liquid.

In the production of tungstic acid, particularly for reduction to metal for processing into lamp filaments, the variables controlling the physical characteristics of the tungstic acid are kept carefully under control, to consistently obtain a standardized type of oxide for reduction to metal. In the disclosure of the present invention, therefore, it is unnecessary to specifically describe this particular phase of the process as it forms no part of the present invention.

The tungstic acid produced in accordance with any preferred prior art practice to obtain material of any desired physical characteristic for reduction to metal, is formed into a slurry in accordance with the invention of the said Driggs patent and silica and potassium chloride in the amounts specified in said Driggs patent are added to the slurry together with iron chloride. The amount of iron chloride added will vary in accordance with the amount of iron desired in the dried tungstic acid. My experiments have indicated that the chart Fig. 7 is substantially correct with respect to the relation between the concentration of iron in the supernatant liquid and the percent of iron adsorbed by the tungstic acid. For convenience the iron percent adsorbed is shown as percent iron (Fe) in the tungsten metal powder after reduction of the oxide by hydrogen.

Referring to the chart, it may be readily noted that when it is desired to introduce .06% Fe in the tungsten metal powder the amount of iron chloride added to the slurry must be such as to provide a concentration of about .125 gram Fe per liter in the supernatant liquor of the slurry. Where .04% Fe is desired in the tungsten metal powder the iron concentration in the supernatant liquid must approximate about .045 gram per liter.

During the reduction of tungstic oxide an average of .01% Fe is generally introduced into the tungsten metal powder due to the use of iron boats. This amount of iron must be allowed for in the practice of the present invention. Accordingly, my preferred practice is to employ an Fe concentration in the supernatant liquor which will give between .04 to .06% Fe in the tungsten metal powder, including any iron introduced under the usual practice.

On pressing this tungsten metal powder into bars and treating according to standard practices heretofore employed in the art, my experiments show that the grain count of the treated metal obtained from metal powder containing from .04% to .06% Fe is from 3 to 4 times that of the same metal powder containing iron less than this amount.

The precise explanation for this unexpected result is not clearly apparent but I believe that iron within this narrow range during sintering either inhibits grain growth during the early stages of heat-treatment or else during the high temperature heat-treatment the volatilization of the iron in excess of the final residual amount of .020 to .035% retained therein interferes with grain growth. The normal iron content of sintered tungsten approximates 0.002% and with this percent of iron the average grain count ranges from about 5000 to 10,000 grains per square millimeter. With iron in the range .020 to .035%, however, a grain count between 15,000 and 20,000 for the same unit area is consistently obtained. This high grain count (small grain size) material containing iron within the range .020–.035% is readily mechanically deformed to wire and filamentary sizes, the iron content thereof, by restraining recrystallization to temperatures above 1600° C. effectively controls the recrystallization of the metal particularly during the early stages of cold working at temperatures approximating but below the recrystallization temperature, thus aiding in the obtainance of a uniform final drawn metal filament.

Although I have described a method of introducing iron into tungsten while the latter is in a slurry as tungstic acid, if desired iron may be introduced into tungsten when the same is in powder form, as by mixing therewith powdered iron, an alloy of iron, or a decomposable iron compound, the proportions being such that iron in the range specified is provided in the finished product.

Having hereinabove described the present invention generically and specifically, it is believed apparent that modifications may be made without essential departure therefrom and all such modifications are contemplated as fall within the scope of the following claims.

I claim:

1. The method of increasing the recrystallization temperature of substantially pure tungsten which comprises incorporating therewith from about .020% to about .035% iron by precipitating tungstic acid, placing thereon water containing an iron compound in solution, reducing said acid to metallic tungsten, and compacting the latter to coherent form.

2. The method of incorporating iron in tungsten which comprises suspending freshly precipitated tungstic acid in water containing a water-soluble and hydrogen-reducible iron compound, permitting the tungstic acid to settle, draining off the supernatant water, drying the tungstic acid, reducing to metal powder, and compacting and treating the powder to form coherent metal.

3. The method of incorporating iron in tungsten which comprises suspending freshly precipitated tungstic acid in water containing a water-soluble and hydrogen-reducible iron compound, permitting the tungstic acid to settle, draining off the supernatant water, drying the tungstic acid, igniting the tungstic acid to oxide, reducing the oxide or tungstic acid to metal powder, and compacting and sintering the powder to form coherent metal.

4. The method of claim 2, wherein the concentration of the iron compound is adjusted with respect to the adsorptive power of the said tungstic acid to obtain an iron content in the said metal powder of from .040% to .060%.

5. The method of claim 2, wherein iron chloride is employed as a water soluble and hydrogen reducible iron compound and the concentration of said iron chloride in the supernatant liquor is adjusted to a concentration of between .045 to .125 gram iron per liter.

6. The method of incorporating iron in tungsten which comprises adding a solution of an iron compound to tungstic acid slurry.

7. The method of producing a tungsten alloy; which, when in severely strain-hardened drawn filamentary form, has the characteristic of inhibited recrystallization at annealing temperatures below about 1600° C., while developing interlocking crystals when subsequently heated to higher temperatures; comprising suspending freshly-precipitated tungstic acid in water containing in solution a hydrogen-reducible iron compound, wherein the concentration of said compound with respect to the absorptive power

of said tungstic acid, is adjusted so that an iron content in the produced metal powder of from .04% to .06% is obtained, allowing the so-impregnated tungstic acid to settle, draining off the supernatant liquid, drying the tungstic acid, reducing it to metal powder, and compacting the powder to form coherent metal.

8. The method of producing filamentary tungsten having an iron content within the range between .020% and .035%, whereby its temperature of recrystallization is increased thereby permitting strain relief to occur during annealing below 1600° C. and allowing said wire to subsequently develop large interlocking crystals when used at higher temperatures, comprising suspending freshly precipitated tungstic acid in water containing in solution a hydrogen-reducible iron compound, in such a concentration that the iron content in the produced metal powder is from .04% to .06%, allowing said tungstic acid to settle, drying, reducing to metal powder, compacting, and working to filamentary form.

9. The method of producing tungsten which has an increased temperature of recrystallization in order to allow strain relief to occur without such recrystallization, which comprises suspending tungstic acid in water containing iron in solution of a concentration sufficient to impregnate the same with an iron content amounting to from .04% to .06% in the metal powder to be produced therefrom, removing and drying said tungstic acid, reducing to metal powder, compacting, and treating to form coherent metal.

10. The method of adding iron to tungsten metal powder, in order to increase the temperature of, and permit strain relief without recrystallization, comprising suspending tungstic acid in an aqueous solution of iron chloride, wherein the concentration of said solution is between .045 and .125 gram per liter to provide an iron content in the metal powder to be produced of from about .04% to .06%, allowing the tungstic acid to settle, and removing, drying and reducing it to metal powder.

WILLIAM C. LILLIENDAHL.

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